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PROCESS FOR THE PRODUCTION OF POROUS PLASTICS AND PRODUCTS

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46 Claims

Matter enclosed in heavy brackets [] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

ABSTRACT OF THE DISCLOSURE

Production of useful shaped articles, formed of porous plastic, by emulsifying droplets of an aqueous medium in an organic liquid containing polymerizable organic compounds(s) and emulsifying agent(s) and, without breaking the dispersed nature of the emulsion, polymerizing it until the organic liquid has been converted to solid form.

The present application is a continuation-in-part of application Ser. No. 45,786, filed July 28, 1960, and entitled, "Production of Cellular Materials From Vinyl-type Resins," now abandoned.

This invention relates to a process for the production of porous plastics and the products produced thereby.

Several methods have been disclosed for the manufacture of porous plastic materials of sponge or foam-like structure. One known method, which is analogous to that used in powder metallurgy sintering, is merely to compact a powdered or granular polymer at a temperature slightly below its melting point. In this way the particles are not fused intimately together but hollow spaces are left in the interstices of the mass.

According to another method, the powdered polymer is mixed with a granular soluble salt, for instance, a water-soluble salt and is heated until it is softened or molten to a compact mass. The soluble salt is then leached from the mass by a solvent, for instance, by water. The remaining product is porous. Its density is dependent on the amount of soluble salt mixed with the polymer prior to heating the same.

It is also known to produce porous plastics by polymerizing a polymerizable compound and subjecting it either during or after its polymerization to the action of gases or of gas-producing compounds. This method suffers, among others, from the drawback that it can be applied but to a relatively small number of plastics, and that it does not allow one to regulate in a simple way the volume ratio of solid substance to pores, as well as the diameter of the individual pores.

It is the object of the present invention to provide a process for the production of porous plastics which process is an improvement over said prior art process.

Another object of the present invention consists in providing a substantially stable composition containing a polymerizable monomer which composition, on subsequent polymerization, yields a porous plastic of improved properties.

A further object of the present invention consists in providing a porous polymer composition the pores of which are filled with a liquid material.

Still another object of the present invention is to provide an improved porous plastic of high strength properties.

Other objects of the present invention and advantageous

features thereof will become apparent as the description proceeds.

In principle the objects of the present invention are achieved by providing a stable water-in-oil emulsion of the following composition:

(1) Water or an aqueous solution containing at least about [40] 25% water forming the dispersed phase; and

(2) A polymerizable organic liquid or a liquid the substantial portions of which consist of a polymerizable organic liquid which contains the following components:

(a) A polymerizable organic liquid consisting of a polymerizable organic compound having a low molecular weight or of several organic compounds of a low molecular weight which are copolymerizable with each other, said liquid being designated as constituent (a); and

(b) At least one organic compound of low molecular weight which is not copolymerizable with the constituent (a) and/or at least one organic compound of high molecular weight which is not copolymerizable with the constituent (a) and/or at least one organic compound of high molecular weight which is copolymerizable with the constituent (a), said organic compound being soluble and contained in solution in the constituent (a) from which solution it is at least partly separated and precipitated at least in the phase boundary by the dispersed phase (1), whereby it acts as an emulsifier, said compound being designated as constituent (b).

(c) If required, at least one organic compound of low molecular weight which is not copolymerizable with the constituent (a) and/or at least one organic compound of high molecular weight which is not copolymerizable with the constituent (a) and/or at least one organic compound of high molecular weight which is copolymerizable with the constituent (a) and which is soluble and contained in solution in the constituent (a), from which solution it is not separated and precipitated at the phase boundary by the dispersed phase (1), may be added. This compound, or compounds, is designated as constituent (c), all of said compounds (a), (b), and (c) forming the continuous phase. The thus composed emulsion is then polymerized in the presence of the usual polymerization initiators and activators to the porous polymer composition the pores of which, depending on the polymerization conditions, may still contain the aqueous liquid initially forming the dispersed phase (1) which [is finally] may be completely or partly eliminated from the thus obtained porous plastics.

In the porous plastics obtained in the afore-mentioned way, the pores are produced by the dispersed phase (1) and the structure of the plastic is produced by the continuous phase (2).

The fundamental discovery of the present invention is that it is possible to form water-in-oil emulsions in which the aqueous phase remains in its dispersed state even during and after the monomer is polymerized. These emulsions can be prepared by making use of microgels acting as the emulsifiers.

These microgels are believed to be peculiar to polymeric systems. When a polymer is dissolved in a solvent, and a non-solvent for said polymer is introduced into said solution, a turbid phase appears to precipitate out of solution. This turbid phase consists of finely divided droplets containing polymer, solvent, and non-solvent, and on further examination these droplets generally prove to be gelatinous. This formation of microgels is fundamentally different from a system which does not contain polymers. For instance, when sugar is in aqueous solution and a non-solvent for sugar is added, the sugar is precipitated in pure form, there being no turbid phase containing sugar, solvent, and non-solvent. For a more detailed explanation of the theory underlying the formation of microgels, reference is made to the textbook, "Principles of Polymer Chemistry" by P. J. Flory,

3

Cornell University Press, Ithaca, New York, 1953, Chapters VIII-3 and XIII.

In the present invention the relationship between the solvent, non-solvent, and polymer or component (b) are extremely important. By varying these relationships, it is possible to produce either sponge-like materials having intercommunicating pores or, on the other hand, foam-like material having isolated non-intercommunicating pores. Before proceeding with a discussion of these different possibilities, attention is directed to the following definitions of solvent, non-solvent, and polymer, as used in the present invention.

A solvent, or component (a) as defined hereinabove, is a liquid in which the polymer, or component (b) as defined hereinabove, is soluble at least to the extent of about 0.5 part, by weight, of the polymer in 100 parts, by weight, of solvent, preferably 2 parts of polymer in 100 parts of solvent.

A non-solvent, or dispersed phase (1) as defined hereinabove, is a liquid in which the polymer has a solubility of less than about 10.0 parts by weight, of polymer, preferably less than 1.0 part in 100 parts of non-solvent. Furthermore, the non-solvent should be soluble in the solvent in a range of about 0.001 part to 20 parts of non-solvent, preferably about 0.005-0.1 part to 100 parts of solvent. (All of the solubilities as described above are those determined at room temperature or, if the monomer is a solid at room temperature, at 100° C.)

According to the process of the present invention porous plastics can be produced in which the volume ratio of solid matter to pores is approximately from 1:0.25 to 1:20 and in which the individual pores have a diameter approximately from 0.1 μ to 600 μ . The volume ratio of solid matter to pores can be regulated in a simple manner by a corresponding selection of the ratio between the compounds forming the continuous phase (2) and the liquid forming the dispersed phase (1), while the diameter of the individual pores can be determined by producing a finer or coarser dispersion of the dispersed phase (1) in the continuous phase (2).

The process according to the present invention for the production of porous plastics must not be confused with the conventional emulsion polymerization processes.

The latter processes are characterized in that an oil-in-water emulsion containing

- (α) water or an aqueous solution as the continuous phase (2),
- (β) a polymerizable organic liquid or a liquid consisting substantially of a polymerizable organic liquid as the dispersed phase (1), and
- (γ) an emulsifier or a mixture of emulsifiers, respectively, and/or a protective colloid or a mixture of protective colloids, respectively,

is polymerized in the presence of polymerization initiators, and, if desired, in the presence of polymerization activators.

In said processes the plastic is obtained in the form of small, noncohesive, compact beads.

The emulsifiers which were used heretofore were soluble in at least one or both of the liquid phases and due to their chemical properties are able to reduce the interfacial surface tension between the water and oil phases. Although some of these emulsifiers can be satisfactorily utilized to form an emulsion of water-in-vinyl-type monomers, it is well known that such emulsions will break on polymerization of the monomer. In other words, prior to the present invention, it was found that the dispersed water phase in a water-in-vinyl-type monomer will coalesce before a solid polymerized structure is formed.

The water-in-oil-emulsions, which are useful in carrying out the process according to the present invention contain, as mentioned under (1), water or substantially water as agent forming the dispersed phase (1).

In general, the dispersed phase (1) is to contain [not

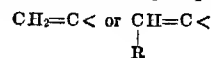
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less than 25] at least about 40% by weight, and preferably not less than 70%, by weight, of water.

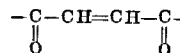
In case the dispersed phase (1) does not exclusively consist of water, it contains, besides water, other additives, which are soluble in water. Examples of such added compounds are alcohols, in particular lower monohydric aliphatic alcohols like methanol, ethanol, n- and iso-propanol, and n-, iso- and tertiary butanol; furthermore lower organic acids like acetic acid and propionic acid, moreover lower ethers and lower ketones like methyl ethyl ether and dimethylketone as well as inorganic salts like sodium chloride, potassium sulfate, sodium sulfate, magnesium sulfate, and magnesium chloride.

Organic liquids with a high dielectric constant like formamide and dimethylformamide, or saccharose, glucose, fructose, or other carbohydrates in aqueous solution may also be used as the dispersed phase (1).

As stated above, the water-in-oil emulsion forming the starting material for producing the porous plastic according to the present invention contains, as principal member of the continuous phase (2) described hereinabove, a polymerizable organic liquid or solvent designated hereinabove as component (a) which is a polymerizable organic liquid consisting of a polymerizable organic compound of low molecular weight or of several organic compounds of low molecular weight that are copolymerizable with each other. The continuous phase should in general contain not less than 10%, by weight, and preferably not less than 45%, by weight, of said constituent (a). It is also possible to use a solution of one or several non-liquid, copolymerizable organic compounds of low molecular weight in one or several liquid copolymerizable organic compounds of low molecular weight. Compounds containing at least one group of the formula



and/or



are particularly suitable as liquid polymerizable compounds of low molecular weight. Examples thereof are compounds which contain, attached to an aromatic nucleus, vinyl or α -alkyl vinyl groups such as styrene, divinyl benzene, o-, m-, p- and α -methyl styrene, furthermore, esters and ethers of vinyl alcohol such as vinyl acetate, divinyl phthalate, divinyl maleate, vinyl butyl ether, divinyl ethanediol ether; additionally, acrylic and methacrylic acid esters such as ethyl acrylate, 1,2-propanediol diacrylate, methyl methacrylate, ethanediol dimethacrylate, butene-2-diol-1,4-dimethacrylate, maleic acid diethyl ester; furthermore unsaturated hydrocarbon halides and cyanides such as vinylidene chloride, allyl chloride, chloroprene acrylonitriles, furthermore unsaturated aliphatic hydrocarbons such as isoprene; as well as the esters and ethers of allyl and methallyl alcohols such as diallyl phthalate, methallyl methyl fumarate, 1,2,3-tri(allyloxy) propane, di-allyl diglycol carbonate, di-allylmaleate.

Suitable for being used as non-liquid polymerizable monomers of low molecular weight are gaseous and solid compounds, for instance, butadiene, vinylchloride, vinyl naphthalene, vinyl carbazole.

The other essential constituent of the continuous phase (2) is the compound (b) which is, as stated above, at least one organic compound of low molecular weight that is not copolymerizable with the constituent (a) and/or at least one organic compound of high molecular weight which is or, respectively, is not copolymerizable with the constituent (a), whereby said constituent (b) must be soluble in the constituent (a) and must, at least partly, be separated and precipitated from said solution at the phase boundary by the constituent of the dispersed phase (1), whereby it acts as an emulsifier.

To find out whether a polymer can be used as constitu-

ent (b), the following simple small-scale test is carried out in the following manner. Either the prospective constituent (b), i.e., the polymer is added to water or the specific aqueous solution of the dispersed phase (1), i.e., the non-solvent whereafter the constituent (a), i.e., the polymerizable monomeric solvent is admixed. Or the prospective constituent (b), i.e., the polymer is first dissolved in the constituent (a), i.e., the polymerizable monomeric solvent, whereafter water or the specific aqueous solution of the dispersed phase (1), i.e., the non-solvent is added. For instance, 1% to 2%, by weight, of the constituent (b) are dissolved in constituent (a) and a few drops of water or of the specific aqueous solution, are added to 10 cc. of said solution of constituent (b) to be tested in constituent (a). The mixture is shaken thoroughly and centrifuged at 2000 revolutions to 3000 revolutions per minute until phase separation takes place. Any compound is suitable for use of constituent (b) in combination with constituent (a) and the aqueous solution (1) which produces in this test a turbid mixture of separation into separate phases. As a rule the more stable water-in-oil emulsions are obtained, the more pronounced is the separation or precipitation of the constituent (b) by the aqueous phase (1).

Suitable compounds (b) are in particular those which contain a major portion of hydrophobic groups and only a minor portion of hydrophilic groups. Such compounds are especially adapted to form the above mentioned microgel. The particular type of microgel which is formed on addition of water or the above mentioned aqueous solution, i.e., the non-solvent (1) to the solution of solvent constituent (a) and polymer constituent (b) is not especially affected by the amount of non-solvent (1). Larger amounts of non-solvent (1) merely result in larger amounts of water-in-oil emulsion. However, the polymerization is very considerably affected by the type of constituent (b) employed.

Suitable representatives of low molecular weight constituents (b) which are not copolymerizable with constituent (a) but are soluble therein and are precipitated from their solutions in constituent (a) by the addition of the aqueous solution (1) are emulsifiers as they are ordinarily employed for preparing water-in-oil emulsions, for instance, esters of higher fatty acids with relatively low molecular polyhydric aliphatic alcohols, esters of higher fatty alcohols with lower and higher fatty acids, amides of higher fatty acids as well as salts of higher alkyl sulfonic acids.

However, the preferred and particularly suitable compounds for use as constituent (b) are polymerization products and polycondensation products which are not at all or only slightly soluble in water and which contain, as hydrophilic groups, carboxyl groups, carboxylate groups, carboxamide groups, hydroxyl groups, ester groups, ether groups, amino groups, ammonium groups, sulfonic acid groups, sulfonate groups, and/or sulfoxide groups.

Such non-copolymerizable compounds of high molecular weight are, for instance, copolymerization products having an acid number of about 8 to 12, of polymerizable carboxylic acids, such as acrylic acid, and hydrophobic polymerizable organic compounds, such as styrene, as well as copolymerization products of said type in which the carboxyl groups are partly or completely neutralized with organic or inorganic bases or are converted into carboxamide group by means of ammonia or amines. Polymerization products and copolymerization products of styrene, of methyl methacrylate, and of vinyl acetate which are prepared by emulsion polymerization in the presence of persulfates and which, therefore, contain sulfonic acid or sulfonate groups, respectively, may be used. Furthermore, for instance, saturated polymerization products and saturated polycondensation products which contain as hydrophilic groups, exclusively or practically exclusively ester and/or ether groups like polymethyl methacrylate and cellulose acetobutyrate may also be used.

Particularly suitable interpolymerizable compounds of high molecular weight are, for instance, polycondensation products of the unsaturated polyester type containing carboxyl groups and/or hydroxyl groups and/or ether groups. Such unsaturated polyesters are composed of polyesters of polybasic, in particular dibasic, carboxylic acids and of polyhydric, in particular dihydric, alcohols. These unsaturated polyesters may also contain the radicals of monovalent carboxylic acids and/or the radicals of monovalent alcohols and/or the radicals of hydroxy carboxylic acids provided such unsaturated polyesters contain polymerizable ethylenically unsaturated groups. Such polyesters are described, for instance, in the book on "Polyesters and Their Applications" by J. Bjorksten, H. Tovey, B. Harker and J. Henning, Reinhold Publishing Corporation, New York.

The polyesters can be prepared, for instance, from their components by a fusion-type condensation or a condensation under azeotropic conditions. Dihydric alcohols, for instance, ethanediol, 1,2-propanediol, 1,3-propanediol, diethylene glycol and 1-allyl-2,3-hydroxypropanediol, in approximately stoichiometric quantities can be converted with α -ethylenically unsaturated dicarboxylic acids such as maleic and fumaric acid, into polyesters suitable as constituent (b). Other unsaturated or saturated dicarboxylic acids, like endomethylene tetrahydrophthalic acid, tetrahydrophthalic acid, *o*-, *m*- and *p*-phthalic acid, succinic acid, and adipic acid, may also be employed as condensation components of the unsaturated polyesters. Furthermore, mono-, tri-, or polybasic carboxylic acids, such as propionic acid, 1,2,4-benzene, tricarboxylic acid, and 1,2,4,5-benzene tetracarboxylic acid and mono-, tri-, or polyhydric alcohols, such as benzyl alcohol, 1,2-di-(allyloxy)-3-propanol. Glycerol, and pentaerythritol as well as hydroxy carboxylic acids, such as 4-hydroxy methyl cyclohexane carboxylic acid can be used as additional components of the unsaturated polyesters.

Particularly stable emulsions are obtained with unsaturated polyesters in which the residual carboxylic groups are partly or completely neutralized with compounds having a basic reaction. Suitable compounds of basic reaction are, for instance, sodium hydroxide, potassium hydroxide, magnesium hydroxide, calcium hydroxide, ammonia, amines such as ethylamine, tri(β -hydroxy ethyl) amine, and α -methyl- β -hydroxy ethylamine, furthermore water-soluble precondensation products of aminoplasts, such as precondensation products of formaldehyde and melamine, formaldehyde and urea, of formaldehyde and dicyandiamide. Thus, to a water-in-oil emulsion containing a polymerizable organic liquid (a) and an unsaturated polyester obtained from unsaturated dicarboxylic acid and polyhydric alcohol as emulsifying agent (b), one may add between about 0.01% and about 15% of the water-soluble preliminary condensation product of melamine and formaldehyde, calculated on the polymerizable organic liquid (a).

There may also be mentioned as copolymerizable compounds of high molecular weight polymerization products containing hydrophilic groups and, in addition, groups which can be further polymerized. Examples of such polymerization products are prepolymerization products from compounds containing hydrophilic groups as well as at least two polymerizable vinylidene groups, such as diallyl phthalate and ethylene glycol dimethacrylate, furthermore precopolymerization products from compounds containing hydrophilic groups as well as at least two polymerizable vinylidene groups and compounds containing one polymerizable vinylidene group such as precopolymerization products from diallyl phthalate and allyl acetate or from ethylene glycol dimethacrylate and methyl methacrylate.

The efficiency of the component (b) as an emulsifier is often increased by adding water-soluble organic compounds of low molecular weight containing a hydrophilic as well as a hydrophobic group additionally to the water

7

forming the dispersed phase (1) of the water-in-oil emulsion. Compounds which are suitable for this purpose are, in particular, alcohols, organic acids, ethers, and ketones as they are mentioned hereinabove as agents forming the dispersed phase (1). It is possible to readily find by means of the above-mentioned small-scale test which agent forming the dispersed phase (1) is particularly suitable for being employed together with given agent (a) and (b) forming the continuous phase (2).

Suitable polymer constituents (b) of the continuous phase (2) have a minimum molecular weight of about 1,000. The preferred molecular weight range is between 20,000 and 200,000.

It has been found that the pH-value of the solvent-polymer-non-solvent system is also of importance. For instance, to form a structure having non-intercommunicating pores, it is necessary that the pH of the non-solvent aqueous solutions be higher than 5.0. An example of this system is: Polymethacrylate as the polymer, styrene as the solvent monomer, and a mixture of ethanol and water as the non-solvent. The microgel which consists of polymethacrylate, styrene, ethanol, and water has an affinity for the ethanol-water non-solvent mixture. This is due to the high concentration of polymethacrylate in the microgel and because said polymer contains ester linkages which are comparatively polar, thereby attracting the polar non-solvent. Similar systems are formed when the non-solvent contains water-soluble vinyl monomers such as acrylic acid, vinyl alcohol and acrylonitrile. These latter systems work especially well in the presence of water-soluble polymerization initiators.

In contrast to porous structures containing non-intercommunicating cells, it is also possible to obtain what may be called a coherent system containing contiguous intercommunicating pores. This structure is obtained when the microgel has a poor affinity for the non-solvent. For instance, when polystyrene prepared by emulsion polymerization and having a molecular weight of at least 10,000 is dissolved in methyl methacrylate, it is precipitated by small amounts of water. The microgel in this case contains a high proportion of polystyrene and therefore, it has a rather low affinity for the non-solvent water. When this system is polymerized with the aid of heat and a soluble peroxide, the water-in-ester emulsion undergoes a phase change at a certain stage of polymerization thereby resulting in a solid polymerization product having a three-dimensional framework, similar to a sponge, containing the non-solvent water throughout.

In these systems wherein water is utilized as the non-solvent, the formation of a coherent mass is favored by pH values lower than 5.

Due to the complexities of the relationship between microgel and non-solvent, it is rather difficult to predict in many cases whether the pores of the polymerization product will be communicating or non-communicating. In general, both types of pores are produced in the polymerization products obtained from water-in-oil emulsions according to the present invention, since a wide range of polarities can be imparted to all the materials used, i.e., the solvent or constituent (a), the polymer or constituent (b), and non-solvent or agent forming the dispersed phase (1). In general, a foam-like, predominantly non-intercommunicating cell structure is obtained by taking care that the interfacial surface tension between the polymer solution in the solvent monomer and the non-solvent is higher than the interfacial surface tension between the solvent monomer and the non-solvent alone. Likewise, if a predominantly coherent plastic is desired, the interfacial surface tension between the polymer solution in the solvent monomer and the non-solvent is preferably lower than the interfacial tension between the solvent monomer and the non-solvent alone.

As stated hereinabove, there may be added, if required, to the monomer constituent (a) and the emulsifying polymer constituent (b) a further constituent (c)

8

which may be an organic compound of low molecular weight that is not copolymerizable with the constituent (a) and/or an organic compound of high molecular weight that is not copolymerizable with the constituent (a) and/or an organic compound of high molecular weight that is copolymerizable with the constituent (a) provided said compounds are soluble in constituent (a) and are not separated or precipitated from said solution at the phase boundary by the agent forming the inner phase (1).

Suitable compounds of low molecular weight of the above mentioned type are, for instance, esters of lower alcohols with lower carboxylic acids or dicarboxylic acids, such as dibutyl phthalate and dimethyl adipate. These compounds can serve as plasticizers for the final porous plastics.

Suitable non-copolymerizable compounds of high molecular weight as mentioned above are in particular homopolymers and copolymers which are free of hydrophilic groups as, for instance, bulk or precipitation polymers of styrene or vinylchloride, which has been prepared by using organic peroxides as polymerization initiators. Such polymers not only affect the properties of the final plastic such as its elasticity, hardness, and inflammability, but also the stability and other properties of the emulsion during its polymerization.

Other suitable copolymerizable substances of high molecular weight useful as constituents (c) are in particular homopolymers and copolymers which are free of hydrophilic groups but still contain vinylidene groups. Examples of such substances are copolymerization products of styrene and butadiene. Such compounds are advantageously used to produce final products with particularly good electrical properties. The water-in-oil emulsions to be used in the process according to the present invention are preferably prepared in the following manner: The constituents (a), (b), and, if required, (c) forming the continuous phase (2) are mixed to form a solution whereupon the aqueous agent forming the dispersed phase (1) is slowly added to said solution while stirring and/or shaking so as to form an emulsion. Thereby, care must be taken that the resulting water-in-oil emulsion is not converted into an oil-in-water emulsion. In some cases it may be necessary to prepare the water-in-oil emulsion in another sequence of steps from its constituents. Thus it is possible first to mix the constituent (a) or the solvent of the continuous phase (2) with the aqueous agent or the non-solvent forming the dispersed phase (1) and thereafter to add the constituent (b) or the polymer or, if required, the constituents (b) and (c) of the continuous phase (2). Usually the emulsions according to the present invention are prepared under atmospheric pressure and at room temperature. However, if desired, it is also possible to operate at higher or lower pressure and/or at higher or lower temperature.

The water-in-oil emulsions according to the present invention contain the constituents forming the continuous phase (2) and the aqueous agent forming the dispersed phase (1) at a volume ratio of from about 1:0.25 to about 1:20, preferably at a volume ratio of from 1:1 to 1:10. The weight ratio of the constituent (a) or solvent of the continuous phase (2) to the constituent (b) or the polymer of the continuous phase (2) is an general between about 1:0.0002 and about 1:0.2, preferably between 1:0.0001 and 1:0.1. However, it may also be increased up to 1:4 if the constituent (b) is an organic substance of a high molecular weight. The weight ratio of the constituent (a) of the continuous phase (2) to the constituent (c) of the continuous phase (2) may range from 1:0 to 1:3.8 provided the weight ratio of the constituent (a) to the sum of the constituents (b) and (c) does not become smaller than 1:4.

In order to prepare porous plastics according to the present invention the resulting water-in-oil emulsions are polymerized. Polymerization may be initiated by admix-

ing water-soluble as well as oil-soluble initiators, or initiators and activators, respectively, preferably at temperatures between about 0° C. and about 100° C. If initiators and activators are jointly used, it may be of advantage that one of these compounds be water-soluble, whereas the other one be soluble in oil. Suitable water-soluble initiators or activators, respectively, are those which are usually employed in emulsion polymerization such as alkali formaldehyde sulfoxylate, persulfates and hydrogen peroxide or, respectively, sodium hydrogen sulfite and cobalt chloride. Suitable oil-soluble initiators or activators, respectively, are also the conventional ones, such as benzoylperoxide, lauroyl peroxide, ethyl methyl ketone peroxide, cyclohexanone peroxide, and azo di-isobutyric acid nitrile, or, respectively, N,N-di-isopropyl-p-toluidine or other tertiary amines and cobalt naphthenate. The initiators and activators are employed in quantities of from 0.1% to 10%, by weight, or, respectively, from 0.01% to 5%, by weight, preferably from 0.5% to 4%, by weight, or, respectively, 0.1% to 4%, by weight, calculated for the total weight of the emulsion. It may be of advantage for increasing the "pot life" of the emulsion by dividing the same in two portions and adding the initiator to the one of said portions and the activator to the other one. Shortly before use the two portions are combined to yield the porous plastic.

The emulsions to which initiators or, respectively, initiators and activators have been added polymerize and harden depending upon their composition, the type and quantity of initiator or, respectively, of initiator and activator added, and the polymerization temperature, within a period of time ranging from a few minutes to several hours and yield porous plastics, the pores of which are filled with water, i.e., the aqueous dispersed phase (1). The water diffuses in the course of time from the resulting porous structures or it is eliminated therefrom by a heat and/or pressure treatment. Although it could be expected that, on polymerization of the above-described water-in-oil emulsion, polymerization products are obtained which contain the aqueous medium or non-solvent forming the dispersed phase (1) in the plastic structure in the form of fine droplets that are not interconnected with each other, the resulting porous plastics have also numerous pores which are interconnected with each other and are open at the surface of the plastic. This phenomenon is probably due to the fact that the water-in-oil emulsion becomes somewhat unstable during the course of the polymerization, so that the individual droplets of the dispersed phase cohere. This is in agreement with the fact that relatively unstable water-in-oil emulsions or emulsions which have been rendered unstable by the admixture of certain additives such as compounds of acid reaction or compounds forming compounds of acid reaction, respectively, for instance, ammonium chloride, sulfuryl chloride, and p-toluene sulfonfyl chloride yield in the course of their polymerization, polymerization products with a pronounced coherence between the individual droplets of the aqueous agent forming the dispersed phase (1).

As has been found, the amount of water added is of considerable importance in the production of a finely porous body on block polymerization of a water-in-oil emulsion according to the present invention. The amount of water required in order to produce a well-drying product can readily be determined by simple preliminary tests. In general said amount should not be less than 25%, by volume, of the total water-in-oil emulsion. Preferably amounts of water ranging from 45% to 95%, e.g. at least 50%, and more advantageously from 60% to 90%, e.g. more than 66%, by volume, calculated for the water-in-oil emulsion are used for carrying out the process according to the present invention.

Drying of the resulting porous polymerized body is considerably improved by employing, as emulsifiers, 75

polymers of high molecular weight which are insoluble or hardly soluble in water, as this has been mentioned hereinabove in connection with the constituent (b). Such polymers are used in amounts between about 0.1% and about 2.5%, and preferably between about 0.3% and about 1.2%, of the polymerizable portion of the mixture, with the water-in-oil emulsion containing at least 50% of said polymerizable organic liquid (a).

The preparation of stable water-in-oil emulsions containing such large amounts of water results in the water being dispersed in the form of spherical droplets having a diameter between less than 1 μ to approximately 50 μ . The spherical shape of the droplets yields cells of highly spherical form which impart to the final porous body an extremely high resistance to compression and which show when compared with foams of the same density obtained by blowing with gases or vapors, a compressive strength that is increased by more than 200%.

According to another embodiment of the present invention compounds capable of generating gases under the polymerization and/or drying conditions, for instance, at increased temperature or decreased pressure may be added to the aqueous phase (1) or the continuous phase (2). Such gas generation may be caused by decomposition of said compound or by the transition of said compound from the dissolved or liquid state into the gaseous state. For instance, the aqueous phase (1) may contain compounds which readily split off carbon dioxide, or relatively readily volatile, water-soluble lipophobic compounds such as carbon dioxide. The constituents of the continuous phase (2) may contain, as blowing agent, relatively readily volatile, hydrophobic substances, for instance, halogenated hydrocarbons, such as 1,1-dichloro-2,2-difluoro ethane. The blowing agent can be added to the emulsion in a conventional manner in the course of its preparation. The amount of blowing agent should not exceed about 20%, by weight, and should preferably be about 10%, by weight, of the total emulsion.

The water-in-oil emulsions as they are employed in the process according to the present invention may contain conventional additives as they are employed in the plastic art, for instance, plasticizers, dyes and pigments, organic and inorganic fillers, agents rendering the plastic thixotropic, fireproofing agents as well as inorganic or organic fibers, fabrics and woven textile materials. The process and products according to the invention can be applied for many products because, on the one hand, most of the known polymerizable monomeric organic compounds can be converted into plastics of known chemical composition and because, on the other hand, the properties of the porous plastics, due to the starting monomers and polymers used, are essentially the same as those of the corresponding non-porous plastics. Therefore, it is possible for a person skilled in the art to predict approximately which properties the individual porous plastics of known chemical composition will have. Hence, it is not difficult for a person skilled in the art to select suitable starting materials for the production of porous plastics of predetermined properties.

In order to produce porous plastic articles according to the process of the present invention, the water-in-oil emulsion can be applied in the required thickness, for instance, to workpieces, materials, and tools of various types made from wood, metal, plastic, rubber, concrete, brickwork, or the like. Coatings may be produced therefrom or sheets, plates, webs or foils, if care is taken, for instance, by employing a mold release compound so that the coating does not firmly adhere to the mold material. The coatings and plates and the like bodies are heat insulating and soundproof and, therefore, of particular importance, for instance, in the building art as flooring, wall and ceiling covering or facing or as supporting building material of light weight. The sheets and foils with intercommunicating cells are useful, for instance, as "breathing" artificial leather, i.e., leather permeable to air

11

or as "breathing" packing material, i.e., packing material which is permeable to air, in particular, if fibers, fabrics or woven textile material or organic materials are employed in the production of such articles. The properties of the resulting artificial leather can be adjusted to those of natural leather by adding hydrophilic fillers thereto. Products obtained according to the process of the present invention are also useful as cork substitute.

Furthermore, it is possible to use the water-in-oil emulsions according to the present invention as adhesives or to produce laminated bodies therefrom in which layers, for instance, from the above-mentioned materials, alternate with layers of porous plastic made from water-in-oil emulsions. Shaped bodies of almost any shape, for instance, flat and corrugated plates, sheets, buttons, structural sections, door frames, pipes, casings, containers, shoe lasts can also be manufactured from such water-in-oil emulsions according to techniques known per se in the manufacture of synthetic resins. Thereby, it is often advantageous to admix fibers and/or organic or inorganic, if desired, expanded filler materials such as mica, lava, pumice, and perlite. Thus, there can be obtained, depending upon the proportion of fibrous materials to emulsion, fibrous articles impregnated with plastics or articles reinforced with fibers, for instance, glass fibers. If filler materials are employed, their amounts added may be not only quite small, but also so large that they are the predominant component of the finished shaped article, for instance, light building plates and that therein the plastic component of the emulsion acts only as binding agent. Finely, porous filters for gases and liquids as well as separators for storage batteries may also be produced by the process according to the present invention. The electrical resistance of such separators is particularly low, if they are manufactured from emulsions containing inorganic salts dissolved in the aqueous agent forming the dispersed phase (1).

In place of fibrous materials such as glass fibers, or, respectively, in addition thereto, there may be embedded in the emulsion according to the present invention reinforcing elements such as metal screens, perforated rubber and plastic plates or sheets, and others.

The emulsions according to the present invention may be polymerized in suitable molds, for instance, by casting. In order to increase the rate of production of such cast articles, a solid polymer either in the form of a powder or in the form of a highly viscous solution, may be obtained prior to the polymerization of the emulsion, thereby increasing the rate of polymerization. Such polymer powders or solutions can be added prior to or subsequent to the emulsifying step. Preferred polymers are the polymerization product of the used monomers, for instance, polymethacrylate when using methacrylate as constituent (a), polystyrene when using styrene as constituent (a), etc.

Thus, an emulsion according to the present invention which will polymerize very rapidly includes a solution of an activator such as a tertiary amine, an emulsifying polymer in a polymerizable monomer, a non-solvent which emulsifies with the latter two ingredients, and a solid polymer mixed with a suitable amount of an initiator such as lauroyl peroxide. Products made from a composition such as the one just mentioned will harden in a relatively short time when heated to a sufficiently high temperature. Furthermore, upon hardening, the mass will be readily separable from the mold due to the fact that water will act as a lubricant and mold release agent on the surface of the cast mass.

When producing cellular plastic with predominantly non-intercommunicating cells, it is possible to produce structural building materials wherein the cells are filled with dyestuffs or with agents protecting against ionizing radiation, and the like. To prevent subsequent escaping and diffusion of the cell contents from the cellular plastic

12

material, it may be provided with a protective coating sealing the cells.

Removal of the aqueous dispersed phase (1) after polymerization from the resulting porous plastic is achieved, for instance, by drying at elevated temperature, in a vacuum, by compressing the plastic, or by allowing it to stand in an air current whereby the water evaporates.

The resulting plastic articles may be rendered substantially fireproof by adding fireproofing agents such as chlorinated paraffins or water soluble salts such as ammonium carbonate thereto.

The hardened plastic articles may be coated, for instance, sprayed with lacquers or coated with metal or the like foils applied thereto by an adhesive.

As stated above, the resulting plastic material can be used for many purposes, for instance, for manufacturing advertising and packing material, toys and household goods, for interior decoration, shop windows, decoration for fair stalls, lamps, furniture, signboards or billboards, orthopedic devices, material for splinting bone fractures and others.

The following examples serve to illustrate the present invention without, however, limiting the same thereto.

Example 1

Two parts, by volume, of styrene containing 2% lauroyl peroxide as polymerization initiator, about 3% of polystyrene of a low intrinsic viscosity, and 0.3% of polymethacrylate are emulsified by stirring with one part, by volume, of a mixture of 20% of ethanol and 80% of water containing 0.01% of acetic acid.

The resulting viscous water-in-oil emulsion is poured in a mold wherein it is polymerized and hardened at a temperature of about 50° C. A solid porous mass, the pores of which are filled with water-ethanol is obtained. The liquid is subsequently evaporated from the pores by standing in air.

Example 2

One part, by volume, of methyl methacrylate containing 0.2% of polystyrene and 2.5% of methyl polymethacrylate is stirred with two parts of an aqueous solution of 0.55% of potassium persulfate, 0.1% of sodium sulfite, and 0.2% of acrylic acid which is adjusted to a pH between 8.0 and 9.0 by the addition of ammonia. The resulting water-in-oil emulsion is heated to a temperature between 70° C. and 80° C. for about half an hour and poured on a plate or in a mold which is also maintained at a temperature between 70° C. and 80° C. After half an hour to two hours, polymerization and hardening is completed and an opaque plastic sheet or molded article is obtained which contains water in finely dispersed mostly non-intercommunicating droplets.

Example 3

One part, by volume, of styrene containing 3% of polyvinyl acetate, 5% of dioctyl phthalate, and 1.5% of cumen peroxide is vigorously shaken with one part of a mixture of ethanol and water (2:1, by volume) which contains 0.05% of disodium saccharate and 0.01% of ferrous sulfate FeSO_4 and has a pH of about 9.0. The resulting water-in-oil emulsion is then heated to a temperature of 60-70° C. while stirring. After the emulsion becomes thick and creamy, it is poured on a plate which is also held at a temperature of about 70° C. A plastic sheet is obtained containing mostly non-intercommunicating droplets of the methanol-water mixture. It is blown up to a foam-like material by heating to a temperature above 130° C.

Example 4

One part, by volume, of a mixture containing 2 parts of acrylonitrile and 1 part of vinylidene chloride, which mixture contains 1% of polystyrene and 1.5% of polymethacrylate is emulsified by stirring with one part of water which contains 1.5% of hydrogen peroxide, 0.2% of glucose, 0.05% of ferrous sulfate, and 0.1% of sodium

13

ethylene diamine tetra-acetate, said aqueous solution being of neutral reaction. After heating the mixture to 40° C. while stirring continuously for about ten minutes, the resulting water-in-oil emulsion is poured on a plate and set in a warm place. A milky plastic sheet is obtained, which can be transformed into a foam-like material by slowly heating the same at a temperature above 170° C. for some time. When the volume of the plastic sheet does not increase any more, the resulting copolymer is cooled rapidly to form a stable foam-like sheet.

Example 5

0.6 part, by weight, of styrene containing, in solution 2% of lauroyl peroxide and 2% of polystyrene and one part, by weight, of a water-ethanol mixture (3:1) are filled in an autoclave provided with a stirring device. Gaseous butadiene is then introduced until 0.4 part, by weight, thereof are absorbed. This mixture is then heated to 35° C. until the pressure decreases to about atmospheric pressure. The autoclave is then opened, and the resulting water-in-oil emulsion is filled in warm molds. After about half an hour, polymerization and hardening is completed. The molds are opened and the resulting porous copolymers are dried in a warm air-stream.

Example 6

In 92.5 g. of methacrylic acid methyl ester as constituent (a) of the compounds of the continuous phase (2) there are dissolved 5 g. of polystyrene produced by emulsion polymerization in the presence of persulfate as constituent (b) of the components of the continuous phase (2) and 3.5 g. of a 50% benzoylperoxide paste. 1.7 g. of dimethyl-p-toluidine and 500 g. of water which forms the dispersed phase (1) are added to said solution while stirring vigorously. The resulting water-in-oil emulsion is stirred at a temperature of 50° C. until a homogeneous [cast] casting mass is formed which is poured into molds and polymerized at a temperature of 50° C. Porous plastic articles are obtained containing water in finely dispersed form. The water can be eliminated on heating at a temperature of 60° C.

Example 7

In 100 cc. of styrene as constituent (a) of the components of the continuous phase (2) there are dissolved 2 g. of polystyrene produced by emulsion polymerization in the presence of persulfate as constituent (b) of the components of the continuous phase (2), 5 cc. of a 60% solution of methyl isobutyl ketone peroxide and 0.3 cc. of a 10% solution of cobalt naphthenate. 60 cc. of said solution are added to 40 cc. of a mixture composed of 93 cc. of water and 7 cc. of isopropanol which mixture forms the dispersed phase (1). The mixture is stirred until a water-in-oil emulsion is formed. The emulsion is polymerized in a mold at a temperature between 70° C. and 90° C. A porous plastic article is obtained from which the components of the dispersed phase (1) can be eliminated by heating at a temperature between 60° C. and 70° C.

Example 8

100 cc. of methyl methacrylate as constituent (a) of the components of the continuous phase (2) are added to 1.6 g. of dimethyl-p-toluidine and then mixed with 100 g. of polymethyl methacrylate as constituent (b) of the components of the continuous phase (2) in which 2 g. of benzoylperoxide are finely dispersed. The mixture is stirred together with 200 cc. of a mixture of 89 cc. of water and 11 cc. of isopropanol which mixture forms the dispersed phase (1) until a water-in-oil emulsion is formed. The emulsion is then polymerized in a mold at a temperature between 40° C. and 50° C. for 10 minutes to 15 minutes. A porous shaped body is obtained from which the aqueous dispersed phase can be expelled by heating at a temperature of 50° C.

14

Example 9

In a mixture consisting of 80 g. of methyl methacrylate and 20 g. of ethylene glycol di-methacrylate as constituent (a) of the components forming the continuous phase (2) there are dissolved 1.8 g. of dimethyl-p-toluidine and 2.5 g. of a copolymerization product of 25% of vinyl acetate and 75% of methyl methacrylate produced by emulsion polymerization in the presence of persulfate as a first portion of the constituent (b) of the components forming the continuous phase (2). The solution is vigorously stirred for 15-20 minutes together with 80 g. of poly-methyl methacrylate as a second portion of said constituent (b) with the addition of 150 cc. of water as the component of the dispersed phase (1). After addition of 2 g. of benzoylperoxide dissolved in 15 cc. of ethyl methacrylate, the resulting water-in-oil emulsion is then applied to a glass fiber fleece which is impregnated therewith by enclosing it between two foils and pressing. Hardening is effected by heating at a temperature of 50° C. for 10 minutes to 15 minutes. A porous plastic plate reinforced by glass fibers is obtained thereby. The water contained therein is evaporated by heating at a temperature between 25° C. and 30° C. within about 24 hours.

Example 10

In a mixture consisting of 90 cc. of styrene and 10 cc. of acrylonitrile as constituent (a) of the components forming the continuous phase (2) there are dissolved 5 cc. of a 60% solution of methyl isobutyl ketone peroxide, 2 g. of polystyrene obtained by emulsion polymerization in the presence of persulfate as a first portion of the constituent (b) of the components forming the continuous phase (2) and 1 cc. of a 10% solution of cobalt naphthenate. 100 cc. of the resulting solution are mixed with 100 cc. of water as the component of the dispersed phase (1) while stirring, until a water-in-oil emulsion is formed. 100 g. of polymethyl methacrylate as a second portion of said constituent (b) are added to said emulsion. The mixture is poured into a mold and polymerized at a temperature between 60° C. and 70° C. A molded body of a porous polymerization product is obtained from which the pore-forming water is evaporated by heating at a temperature of 20-25° C. for several hours.

Example 11

To a mixture consisting of 65 g. of an unsaturated polyester of the acid number 40 prepared from maleic acid, phthalic acid, and propylene glycol at a molar ratio of 2:1:3.3 as constituent (b) of the components forming the continuous phase (2) and 35 g. of styrene as constituent (a) of the components forming the continuous phase (2) there are added 2 g. of benzoylperoxide and, thereafter, slowly 100 cc. of water as component forming the dispersed phase (1). The mixture is vigorously stirred at a temperature of 10° C. until a water-in-oil emulsion is formed. The emulsion is mixed with 0.18 g. of dimethyl-p-toluidine, poured on a glass plate to form a layer of the desired uniform thickness, for instance, between 1 mm. and 15 mm. and polymerized and hardened by heating at a temperature of 30° C. for 10 minutes. The water can be evaporated from the resulting porous plates by heating at a temperature between 80° C. and 100° C.

Example 12

65 g. of the unsaturated polyester described in Example 11 as a first portion of the constituent (b) of the components forming the continuous phase (2) as well as 1.5 g. of a copolymerization product of the acid number 10 prepared from styrene and acrylic acid as a second portion of said constituent (b) are dissolved in 65 g. of

(a) A mixture of diallyl phthalate and styrene at a ratio of 1:3, by weight, or

(b) In 65 g. of allylchloride, or

15

(c) In 65 g. of vinylacetate.

The compounds mentioned under (a), (b), and (c) hereinabove are the constituents (a) of the components of the continuous phase (2).

To each of these solutions there are added 100 cc. of water as component of the dispersed phase (1) after the addition of 2 g. of benzoylperoxide. The mixtures are then emulsified by stirring vigorously. Each of the resulting emulsions is mixed with 0.18 g. of dimethyl-p-toluidine, poured on a glass plate to form layers of uniform thickness, and polymerized and hardened at temperatures of 60-70° C. Porous plastic sheets and plates are obtained thereby.

Example 13

A prepolymerization product of sirupy consistency as constituent (b) of the components forming the continuous phase (2) as it is obtained from 70 g. of methyl methacrylate, which still contains monomeric methyl methacrylate as constituent (a) of the components forming the continuous phase (2) is thoroughly mixed with 16.5 g. of ethylene glycol di-methylacrylate, 4.0 g. of a paste containing 50% of benzoylperoxide, and 10.0 g. of polyvinylchloride powder as constituent (c) of the components forming the continuous phase (2). The mixture is stirred with 100 g. of water as component forming the dispersed phase (1) until a water-in-oil emulsion is formed. The emulsion is allowed to stand for some time for the purpose of de-aeration, whereafter 1.5 g. of dimethyl-p-toluidine are added. It is spread in the desired thickness, for instance, of 5 mm. to 10 mm. onto a flat surface. The resulting coating is polymerized at a temperature of 60° C. for 10 minutes to 15 minutes. The water is allowed to evaporate by standing at a temperature of 20° C.

Example 14

To a mixture consisting of 65.0 g. of the unsaturated polyester described in Example 11 as constituent (b) of the components forming the continuous phase (2) and 35.0 g. of styrene as constituent (a) of the components forming the continuous phase (2) there are added 4.0 g. of a paste containing 50% of benzoylperoxide as well as 5.0 g. of polyvinylchloride powder as constituent (c) of the components forming the continuous phase (2). The resulting mixture is stirred together with 150 g. of water as component forming the dispersed phase (1) until a water-in-oil emulsion is formed. After its de-aeration it is mixed with 30.0 g. of styrene and 0.8 g. of dimethyl-p-toluidine, poured into molds, and polymerized and hardened at a temperature of 20° C. A porous shaped body is obtained from which the water is eliminated by heating to 100° C.

Example 15

A mixture is prepared from 35.0 g. of styrene, 25.0 g. of isoprene, both being the constituents (a) of the components forming the continuous phase (2), 60 g. of the unsaturated polyester described in Example [6] 11 to which 2.0 g. of benzoyl peroxide and 3.0 g. of triethanolamine are added to cause salt formation, said polyester salt being the constituent (b) of the components forming the continuous phase (2). The mixture is stirred together with 0.5 g. of dimethyl-p-toluidine and 80.0 g. of water as component forming the dispersed phase (1) until a water-in-oil emulsion is formed. Said emulsion is poured into molds and is polymerized and hardened at 25° C. The water is eliminated from the resulting porous shaped article by heating at a temperature of 100° C.

Example 16

A mixture consisting of 75.0 g. of diallyl phthalate and 25.0 g. of methyl methacrylate, both being the constituent (a) of the components forming the continuous phase (2) is mixed with 2.0 g. of benzoylperoxide, 1.5 g. of dimethyl

16

product from diallyl phthalate as constituent (b) of the components forming the continuous phase (2). The mixture is stirred together with 75.0 g. of water as component forming the dispersed phase (1) until a water-in-oil emulsion is formed. The resulting emulsion is poured into molds at a temperature of 50° C. and is polymerized. Thereafter, the water is eliminated from the resulting porous shaped bodies by heating at 100° C.

Example 17

To 93.0 g. of methyl methacrylate as constituent (a) of the components forming the continuous phase (2) there are added 5.0 g. of polystyrene produced by emulsion polymerization in the presence of persulfate, said polystyrene being the constituent (b) of the components forming the continuous phase (2), 2.0 g. of benzoyl peroxide, 1.5 g. of dimethyl-p-toluidine and 100.0 g. of a copolymerization product powder as filler as it is obtained from 40 parts of styrene and 60 parts of the unsaturated polyester described in Example 11. The mixture is stirred with 150 g. of water as component forming the dispersed phase (1), until a water-in-oil emulsion is formed. The emulsion is poured into molds and polymerized and hardened at a temperature of 50° C. The water is eliminated from the obtained porous shaped bodies by heating to 100° C.

Example 18

10 g. of benzoylperoxide are dissolved in 500 g. of an unsaturated polyester as described in Example 11 and 167 g. of styrene. 600 g. of water are slowly and gradually added to said solution at 5-10° C. while stirring until a white, creamy water-in-oil emulsion is formed. A solution of 0.8 g. of dimethyl-p-toluidine in 100 g. of styrene is stirred into said emulsion. The resulting fluid emulsion is cast into plate molds in a thickness of about 5 mm. The mold is exposed in a water bath to a temperature of 50° C. The cast resin polymerizes and hardens within about 10 minutes to 15 minutes. The water is removed from the porous plastic plates by heating to 100° C. The resulting plates have a density of 0.6.

Example 19

In place of styrene as used in Example 18, there is employed the same amount of methyl methacrylate while the other components, catalysts, emulsifying procedure, polymerization conditions, and removal of the water proceed in the same manner as described in said Example 18. A finely porous molded article of a density of 0.6 is obtained.

It may be mentioned that water-soluble protective colloids and surface-active agents must not be present in the emulsions because such protective colloids and surface-active agents would prevent formation of water-in-oil emulsions as they are required in accordance with the present invention.

The amount of non-solvent or component forming the dispersed phase, i.e., of water or an aqueous liquid, is chosen so that it corresponds to the desired total pore volume and thus permits exact adjustment of said pore volume. Although the resulting porous plastic bodies are of considerable porosity, they still show smooth or bright surfaces depending upon the mold walls.

The use of water as pore-forming component has considerable advantages. It prevents excessive overheating, even when the polymerization proceeds strongly exothermically, especially when using rapid activators. The polymerization heat can be dissipated more readily. Thus it is possible to produce molded bodies of large size without any excessive expansion of the polymerization product. The volume of the resulting plastic body varies only slightly with respect to the starting volume of the water-in-oil emulsion. Shrinkage is insignificant. The molded bodies are readily released from the molds or

17

from surfaces on which they were cast due to the formation of a water film or of water vapors.

As stated above, the breathing activity of plates, sheets, coatings, foils made according to the present invention is excellent. The same is true with respect to their sound-absorbing and heat-insulating properties. The new plastics have very good elasticity properties and exhibit all the other working and processing advantages of plastics over other materials such as wood. Due to their fine porosity they can readily be drilled or nailed. They are especially valuable as leather substitute. The preferred leather substitute material is composed of the porous polymerization product of styrene or methyl methacrylate with an unsaturated polyester as constituent (b) of the continuous phase (2).

Of course, many changes and variations may be made in the composition of the various components of the water-in-oil emulsions, in their polymerization, the removal of the dispersed phase (1) therefrom and the like in accordance with the principles set forth herein and in the claims annexed hereto.

I claim:

1. A method of producing solid materials having a plurality of droplets dispersed therein, which method comprises forming a stable water-in-oil emulsion composed of water, methyl-methacrylate, as the oil phase, and polystyrene having a molecular weight of at least 10,000 as the emulsifier, and polymerizing the methyl-acrylate to form polymethylmethacrylate without breaking the dispersed nature of the emulsion, thereby forming solid polymethylmethacrylate having a plurality of water droplets dispersed therein.

2. A method of producing solid materials having a plurality of droplets dispersed therein, which method comprises forming a stable water-in-oil emulsion composed of water, styrene, as the oil phase, and polystyrene, as the emulsifier; and polymerizing the styrene to form polystyrene without breaking the dispersed nature of the emulsion, thereby forming a solid plastic material having a plurality of water droplets dispersed therein.

3. A method of producing solid materials having a plurality of droplets dispersed therein, which method comprises forming a stable water-in-oil emulsion composed of water, a mixture of styrene and acrylonitrile, as the oil phase, and polystyrene, as the emulsifier; and polymerizing the mixture of styrene and acrylonitrile to form a copolymerization product therefrom without breaking the dispersed nature of the emulsion, thereby forming a solid plastic material having a plurality of water droplets dispersed therein.

4. A method of producing solid materials having a plurality of droplets dispersed therein, which method comprises forming a stable water-in-oil emulsion composed of water, styrene, as the oil phase, and an unsaturated polyester obtained from maleic acid, phthalic acid, and propylene glycol, as the emulsifier; and polymerizing the styrene to form polystyrene without breaking the dispersed nature of the emulsion, thereby forming a solid plastic material having a plurality of water droplets dispersed therein.

5. A method of producing solid materials having a plurality of droplets dispersed therein, which method comprises forming a stable water-in-oil emulsion composed of water, styrene, as the oil phase, an unsaturated polyester obtained from maleic acid, phthalic acid and propylene glycol, as the emulsifier, and polyvinylchloride powder; and polymerizing the styrene to form polystyrene without breaking the dispersed nature of the emulsion, thereby forming a solid plastic material having a plurality of water droplets dispersed therein.

6. A method of producing solid materials having a plurality of droplets dispersed therein, which method comprises forming a stable water-in-oil emulsion composed of

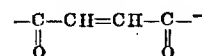
(1) an aqueous medium selected from the group con-

18

sisting of water and aqueous solutions of water-soluble alcohols, lower organic acids, lower alkanones, alkali metal salts, and magnesium salts, said aqueous medium forming the aqueous dispersed phase, said aqueous solutions containing at least about 25% by weight, of water,

(2) as dispersion medium, an organic liquid containing

(a) a polymerizable organic liquid selected from the group consisting of a polymerizable compound having at least one ethylenically unsaturated group [a polymerizable compound having at least one group of the formula



and copolymerizable mixtures thereof, said polymerizable organic liquid forming the oil phase; and

(b) a substantially water-insoluble polymeric compound being soluble in said polymerizable organic liquid, said compound being selected from the group consisting of substantially water-insoluble polymerization products, [substantially water-insoluble polycondensation products, substantially water-insoluble unsaturated polyesters obtained from unsaturated polycarboxylic acids and polyhydric alcohols] and mixtures thereof, said polymeric compounds containing hydrophilic groups in an amount insufficient to essentially increase their solubility in water, said polymeric compound forming the emulsifying agent on contact with said aqueous medium;

and polymerizing the polymerizable organic liquid in said water-in-oil emulsion to form the respective polymerization product without breaking the dispersed nature of the emulsion, thereby forming a solid plastic material having a plurality of water droplets dispersed therein.

7. A process for the production of porous plastics, which process comprises forming a stable water-in-oil emulsion containing

(1) an aqueous medium selected from the group consisting of water and an aqueous solution, said aqueous medium being the agent forming the dispersed phase, said aqueous solution containing at least about 25%, by weight, of water, and

(2) as dispersion medium, an organic liquid containing

(a) a polymerizable organic liquid selected from the group consisting of a polymerizable organic compound and at least two such organic compounds being co-polymerizable with each other;

(b) at least one organic compound being co-polymerizable with said polymerizable organic liquid (a), said organic compound being soluble in and being contained in solution by said polymerizable organic liquid (a) and being at least partly separated from said solution at the phase boundary by addition thereto of said aqueous medium (1), thereby acting as an emulsifier; and

(c) at least another organic compound being soluble in and contained in solution by said polymerizable organic liquid (a) and not being separated from said solution at the phase boundary by the addition of said aqueous medium (1), said organic liquid (2) forming the continuous phase,

polymerizing said water-in-oil emulsion in the presence

19

of conventional polymerization initiators as well as conventional polymerization activators without breaking the water-in-oil emulsion, and, at least partly, removing the aqueous medium (1) from the resulting porous plastic.

8. The process according to claim 7, wherein the resulting water-in-oil emulsion contains at least 50%, by volume, of water.

9. The process according to claim 7, wherein the resulting water-in-oil emulsion contains more than 66%, by volume, of water.

10. The process according to claim 7, wherein the aqueous medium is an aqueous solution of an inorganic salt.

11. The process according to claim 7, wherein the spherical droplets of water contained in the resulting water-in-oil emulsion have a diameter not exceeding 50 μ .

12. The process according to claim 7, wherein the polymerizable organic liquid (a) is a compound selected from the group consisting of styrene, an acrylic acid ester, a methacrylic acid ester, and a mixture thereof.

13. The process according to claim 7, wherein the organic compound (b) is an unsaturated polyester, the free carboxyl groups of which are at least partly neutralized by a compound of basic reaction.

14. The process according to claim 7, wherein fillers, fibrous materials, and reinforcing agents are added to the water-in-oil emulsion.

15. The process according to claim 7, wherein between 0.01% and about 15%, calculated for the polymerizable organic liquid (a), of the water soluble preliminary condensation product of melamine and formaldehyde are added to the water-in-oil emulsion containing a polymerizable vinyl compound as polymerizable organic liquid (a) and an unsaturated polyester obtained from an unsaturated dicarboxylic acid and a polyhydric alcohol as emulsifying agent (b), said unsaturated polyester being soluble in and dissolved by said polymerizable vinyl compound.

16. The process according to claim 7, wherein between about [0.05%] 0.1% and about 2.5%, calculated for the polymerizable portion of the water-in-oil emulsion of the emulsifying agent (b) consisting of a polymerization product of high molecular weight being soluble in the water-insoluble polymerizable ethylenically unsaturated organic liquid (a), and at least 50% of said polymerizable organic liquid (a) are present in said water-in-oil emulsion.

17. The process according to claim 16, wherein between about 0.3% and about 1.2%, calculated for the polymerizable portion of the water-in-oil emulsion of the emulsifying agent (b) consisting of a polymerization product of high molecular weight being soluble in the water-insoluble polymerizable ethylenically unsaturated organic liquid (a), and at least 50% of said polymerizable organic liquid (a) are present in said water-in-oil emulsion.

18. The porous plastic produced by the process of claim 7.

19. A method of producing porous plastic shaped products, which method comprises forming a stable water-in-oil emulsion composed of water, methylmethacrylate, as the oil phase, and polystyrene having a molecular weight of at least 10,000 as the emulsifier, shaping the emulsion to the desired product, polymerizing the methylmethacrylate to form polymethylmethacrylate without breaking the dispersed nature of the emulsion, thereby forming the solid shaped polymethylmethacrylate product having a plurality of water droplets dispersed therein, and at least partly removing the water from the resulting product.

20. A method of producing porous plastic shaped products which method comprises forming a stable water-in-oil emulsion composed of water, styrene as the oil phase and polystyrene as the emulsifier, shaping the emulsion to the desired product, polymerizing the styrene to form

20

polystyrene without breaking the dispersed nature of the emulsion, thereby forming the solid shaped plastic product having a plurality of water droplets dispersed therein, and at least partly removing the water from the resulting product.

21. A method of producing porous plastic shaped products, which method comprises forming a stable water-in-oil emulsion composed of water, a mixture of styrene and acrylonitrile as the oil phase, and polystyrene as the emulsifier, shaping the emulsion to the desired product, polymerizing the mixture of styrene and acrylonitrile to form a copolymerization product therefrom without breaking the dispersed nature of the emulsion, thereby forming the solid shaped plastic product having a plurality of water droplets dispersed therein, and at least partly removing the water from the resulting product.

22. A method of producing porous plastic shaped products, which method comprises forming a stable water-in-oil emulsion composed of water, styrene as the oil phase, and an unsaturated polyester obtained from maleic acid, phthalic acid, and propylene glycol as the emulsifier, shaping the emulsion to the desired product polymerizing the styrene to form polystyrene without breaking the dispersed nature of the emulsion, thereby forming the solid shaped plastic product having a plurality of water droplets dispersed therein, and at least partly removing the water from the resulting product.

23. A method of producing porous plastic shaped products, which method comprises forming a stable water-in-oil emulsion composed of water, styrene as the oil phase, an unsaturated polyester obtained from maleic acid, phthalic acid, and propylene glycol as the emulsifier, and polyvinylchloride powder, shaping the emulsion to the desired product, polymerizing the styrene to form polystyrene without breaking the dispersed nature of the emulsion, thereby forming the solid shaped plastic product having a plurality of water droplets dispersed therein, and at least partly removing the water from the resulting product.

24. A method of producing porous plastic shaped products, which method comprises forming a stable water-in-oil emulsion composed of

- (1) an aqueous medium forming the aqueous dispersed phase and
- (2) as dispersion medium, an organic liquid containing
 - (a) a polymerizable organic liquid forming the oil phase and
 - (b) an emulsifying agent,

shaping the emulsion to the desired product, polymerizing the polymerizable organic liquid in said water-in-oil emulsion to form the respective polymerization product without breaking the dispersed nature of the emulsion, thereby forming the solid shaped plastic product having a plurality of water droplets dispersed therein, and at least partly removing the water from the resulting product.

25. A method of producing porous plastic shaped products, which method comprises forming a stable water-in-oil emulsion composed of

- (1) an aqueous medium forming the aqueous dispersed phase and
- (2) as dispersion medium, an organic liquid containing
 - (a) a polymerizable organic liquid forming the oil phase and
 - (b) an emulsifying agent,

the water content of said water-in-oil emulsion being between about 25% and about 95%, shaping the emulsion to the desired product, polymerizing the polymerizable organic liquid in said water-in-oil emulsion to form the respective polymerization product without breaking the dispersed nature of the emulsion, thereby forming the solid shaped plastic product having a plurality of water

21

droplets dispersed therein, and at least partly removing the water from the resulting product.

26. The porous plastic shaped product produced by the [process] method of claim 24.

27. A method in accordance with claim 24 wherein said emulsifying agent (b) includes an unsaturated polyester, the free carboxyl groups of which have at least partly been converted to salts.

28. A method in accordance with claim 24 wherein said emulsion contains reinforcing fibers.

29. A method in accordance with claim 24 wherein said emulsion is shaped in a mold having the shape of a useful object and polymerized therein.

30. A method in accordance with claim 24 wherein said aqueous medium is present in said emulsion in the form of droplets having a diameter not exceeding 50 μ .

31. A method in accordance with claim 24 wherein said dispersion medium includes a water-insoluble organic compound having more than one polymerizable ethylenically unsaturated group.

32. A method in accordance with claim 24 wherein said emulsifying agent includes a polymeric compound which has hydrophilic groups and will form a turbid phase or precipitate when a solution of said compound in said dispersion medium is contacted with said aqueous medium, the amount of said hydrophilic group being insufficient to increase the solubility of said polymeric compounds to the extent that they become essentially soluble in water.

33. A method in accordance with claim 24 wherein said aqueous phase is a solution of ethanol in water, said emulsifying agent (b) is polystyrene, said polymerization is continued until the water-in-oil emulsion is hardened to a solid shaped plastic product having a plurality of droplets of said solution dispersed therein in contiguous intercommunicating pores, and at least part of the solution is removed by exposing said product to air at room temperature.

34. A method of producing solid materials having a plurality of droplets dispersed therein, which method comprises forming a stable water-in-oil emulsion composed of

- (1) an aqueous medium selected from the group consisting of water and aqueous solutions of water-soluble alcohols, lower organic acids, lower alkanones, alkali metal salts, and magnesium salts said aqueous medium forming the aqueous dispersed phase, said aqueous solutions containing at least about 40% by weight, of water,

- (2) as dispersion medium, an organic liquid containing

- (a) a polymerizable organic liquid selected from the group consisting of a polymerizable compound having at least one ethylenically unsaturated group and copolymerizable mixtures thereof, said polymerizable organic liquid forming the oil phase; and

- (b) a substantially water-insoluble polymeric compound being soluble in said polymerizable organic liquid, said compound being selected from the group consisting of substantially water-insoluble polymerization products, and mixtures thereof, said polymeric compounds containing hydrophilic groups in an amount insufficient to essentially increase their solubility in water, said polymeric compound forming the emulsifying agent on contact with said aqueous medium;

and polymerizing the polymerizable organic liquid in said water-in-oil emulsion to form the respective polymerization product without breaking the dispersed nature of the emulsion, thereby forming a solid plastic material having a plurality of water droplets dispersed therein.

35. A method in accordance with claim 34 wherein said emulsifying agent (b) includes an unsaturated poly-

22

ester, the free carboxyl groups of which have at least partly been converted to salts.

36. A method in accordance with claim 34 wherein said emulsion contains reinforcing fibers.

37. A method in accordance with claim 34 wherein said emulsion is shaped in a mold having the shape of a useful object and polymerized therein.

38. A method in accordance with claim 34 wherein said aqueous medium is present in said emulsion in the form of droplets having a diameter not exceeding 50 μ .

39. A method in accordance with claim 34 wherein said dispersion medium includes a water-insoluble organic compound having more than one polymerizable ethylenically unsaturated group.

40. A method of producing solid materials having a plurality of droplets dispersed therein, which method comprises forming a stable water-in-oil emulsion composed of

- (1) an aqueous solution of water-soluble magnesium salt forming the aqueous dispersed phase, said aqueous solution containing at least about 40% by weight, of water,

- (2) as dispersion medium, an organic liquid containing

- (a) polymerizable organic liquid selected from the group consisting of a polymerizable compound having at least one ethylenically unsaturated group and copolymerizable mixtures thereof, said polymerizable organic liquid forming the oil phase; and

- (b) substantially water-insoluble polymeric compound being soluble in said polymerizable organic liquid, said compound being selected from the group consisting of substantially water-insoluble polymerization products, and mixtures thereof, said polymeric compounds containing hydrophilic groups in an amount insufficient to essentially increase their solubility in water, said polymeric compound forming an emulsifying agent on contact with said solution;

and polymerizing the polymerizable organic liquid in said water-in-oil emulsion to form the respective polymerization product without breaking the dispersed nature of the emulsion, thereby forming a solid plastic material having plurality of water droplets dispersed therein.

41. A method of producing solid materials having a plurality of droplets dispersed therein, which method comprises forming a stable water-in-oil emulsion composed of

- (1) an aqueous solution of water-soluble alkali metal salt forming the aqueous dispersed phase, said aqueous solution containing at least about 40% by weight, of water,

- (2) as dispersion medium, an organic liquid containing

- (a) polymerizable organic liquid selected from the group consisting of a polymerizable compound having at least one ethylenically unsaturated group and copolymerizable mixtures thereof, said polymerizable organic liquid forming the oil phase; and

- (b) substantially water-insoluble polymeric compound being soluble in said polymerizable organic liquid, said compound being selected from the group consisting of substantially water-insoluble polymerization products, and mixtures thereof, said polymeric compounds containing hydrophilic groups in an amount insufficient to essentially increase their solubility in water, said polymeric compound forming an emulsifying agent on contact with said solution;

and polymerizing the polymerizable organic liquid in said water-in-oil emulsion to form the respective polymerization product without breaking the dispersed nature of the

23

emulsion, thereby forming a solid plastic material having a plurality of water droplets dispersed therein.

42. A method of producing solid materials having a plurality of droplets dispersed therein, which method comprises forming a stable water-in-oil emulsion composed of

- (1) an aqueous solution of water-soluble lower alkanone forming the aqueous dispersed phase, said aqueous solution containing at least about 40% by weight, of water,
- (2) as dispersion medium, an organic liquid containing

- (a) polymerizable organic liquid selected from the group consisting of a polymerizable compound having at least one ethylenically unsaturated group and copolymerizable mixtures thereof, said polymerizable organic liquid forming the oil phase; and

- (b) substantially water-insoluble polymeric compound being soluble in said polymerizable organic liquid, said compound being selected from the group consisting of substantially water-insoluble polymerization products, and mixtures thereof, said polymeric compounds containing hydrophilic groups in an amount insufficient to essentially increase their solubility in water, said polymeric compound forming an emulsifying agent on contact with said solution;

and polymerizing the polymerizable organic liquid in said water-in-oil emulsion to form the respective polymerization product without breaking the dispersed nature of the emulsion, thereby forming a solid plastic material having a plurality of water droplets dispersed therein.

43. A method of producing solid materials having a plurality of droplets dispersed therein, which method comprises forming a stable water-in-oil emulsion composed of

- (1) an aqueous solution of water-soluble lower organic acid forming the aqueous dispersed phase, said aqueous solution containing at least about 40% by weight, of water,
- (2) as dispersion medium, an organic liquid containing

- (a) polymerizable organic liquid selected from the group consisting of a polymerizable compound having at least one ethylenically unsaturated group and copolymerizable mixtures thereof, said polymerizable organic liquid forming the oil phase; and

- (b) substantially water-insoluble polymeric compound being soluble in said polymerizable organic liquid, said compound being selected from the group consisting of substantially water-insoluble polymerization products, and mixtures thereof, said polymeric compounds containing hydrophilic groups in an amount insufficient to essentially increase their solubility in water, said polymeric compound forming an emulsifying agent on contact with said solution;

and polymerizing the polymerizable organic liquid in said water-in-oil emulsion to form the respective polymerization product without breaking the dispersed nature of the emulsion, thereby forming a solid plastic material having a plurality of water droplets dispersed therein.

44. A method of producing solid materials having a plurality of droplets dispersed therein, which method comprises forming a stable water-in-oil emulsion composed of

- (1) an aqueous solution of water-soluble alcohols forming the aqueous dispersed phase, said aqueous solution containing at least about 40% by weight, of water,
- (2) as dispersion medium, an organic liquid containing

- (a) polymerizable organic liquid selected from

24

the group consisting of a polymerizable compound having at least one ethylenically unsaturated group and copolymerizable mixtures thereof, said polymerizable organic liquid forming the oil phase; and

- (b) substantially water-insoluble polymeric compound being soluble in said polymerizable organic liquid, said compound being selected from the group consisting of substantially water-insoluble polymerization products, and mixtures thereof, said polymeric compounds containing hydrophilic groups in an amount insufficient to essentially increase their solubility in water, said polymeric compound forming an emulsifying agent on contact with said solution;

and polymerizing the polymerizable organic liquid in said water-in-oil emulsion to form the respective polymerization product without breaking the dispersed nature of the emulsion, thereby forming a solid plastic material having a plurality of water droplets dispersed therein.

45. A method of producing solid materials having a plurality of droplets dispersed therein, which method comprises forming a stable water-in-oil emulsion composed of

- (1) water forming the aqueous dispersed phase;
- (2) as dispersion medium, an organic liquid containing

- (a) polymerizable organic liquid selected from the group consisting of a polymerizable compound having at least one ethylenically unsaturated group and copolymerizable mixtures thereof, said polymerizable organic liquid forming the oil phase; and

- (b) substantially water-insoluble polymeric compound being soluble in said polymerizable organic liquid, said compound being selected from the group consisting of substantially water-insoluble polymerization products, and mixtures thereof, said polymeric compounds containing hydrophilic groups in an amount insufficient to essentially increase their solubility in water, said polymeric compound forming an emulsifying agent on contact with said water;

and polymerizing the polymerizable organic liquid in said water-in-oil emulsion to form the respective polymerization product without breaking the dispersed nature of the emulsion, thereby forming a solid plastic material having a plurality of water droplets dispersed therein.

46. The process according to claim 7 wherein said aqueous solution contains at least about 40% by weight, of water.

References Cited

The following references, cited by the Examiner, are of record in the patented file of this patent or the original patent.

UNITED STATES PATENTS

2,473,801	6/1949	Kropa.
2,505,353	4/1950	Fisk.
2,726,177	12/1955	Lew.
2,739,909	3/1956	Rosenthal.
2,843,556	7/1958	Moorman.
1,967,220	7/1934	Barret et al.
2,016,199	10/1935	Howard.
2,112,529	3/1938	Hazell.
2,120,935	6/1938	Groff.
2,220,685	11/1940	Myers.
2,327,968	8/1943	Ripper.
2,443,735	6/1948	Kropa.
2,533,270	12/1950	Linkletter.
2,655,496	10/1953	Adams.
2,864,777	12/1958	Greenhoe.
2,912,399	11/1959	Bartil.

(Additional references on following page)

27,444

25

UNITED STATES PATENTS

2,947,735	8/1960	Bartl.	
3,206,441	9/1965	Von Bonin.	
3,284,393	11/1966	Vanderhoff et al.	
2,700,026	1/1955	Dibert	260—29.6
2,872,423	2/1959	Goldstein	260—29.6

FOREIGN PATENTS

558,970	1/1957	Belgium.
565,530	1/1958	Belgium.
763,396	12/1956	Great Britain.

26

OTHER REFERENCES

Wenning: Makromolekular-Chemie, 1956, pp. 196—213.

JOHN C. BLEUTGE, Primary Examiner

U.S. CL. X.R.

117—126 GB, 132 C, 135.5, 138.8 UA, 161 K, 161 UZ;
136—146; 252—62; 260—2.5 N, 17.4 R, 17.4 GC, 29.4
10 UA, 851, 855, 856, 861, 872, 873, 881, 884, 885, 886

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3,055,966

MICROPOROUS MATERIAL SEPARATOR AND METHOD OF MAKING SEPARATOR

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10 Claims. (Cl. 136-146)

This invention relates to microporous plates and more particularly to such plates which may be advantageously used as separators or diaphragms between the electrodes of electric batteries or accumulators.

One requisite of a separator for an electric accumulator is a high degree of microporosity to allow diffusion of the electrolyte and free movement of ions. The pore size of the separator must be small enough to prevent conductive particles from the electrode plates from penetrating the separators and in that way causing shortcircuiting between said electrode plates.

Other requisites are low, uniform and unchangeable electrical resistance, good chemical resistance against the powerful oxidizing attacks to which separators in electric accumulators are exposed during excessive rates of charge and discharge, and sufficient strength and toughness to withstand handling and to maintain the shape of the separator when wet.

The surface of a microporous sheet suitable as a separator between electrode plates in an electric accumulator should have a low friction coefficient and a good wearing resistance and solidity in order not to become destroyed through movement of the electrodes relative the separators. Such a movement, though with small amplitude, occurs especially in batteries for traction type vehicles. Additionally, increasing mechanical pressure is applied to separators when tightly assembled in an accumulator cell together with electrodes in consequence of the growing thickness of the latter during service.

The provision of satisfactory separators for electric accumulators presents increasing problems primarily due to recent advancements in the battery art. Wood separators, which earlier have been successfully employed, are in many cases unsuitable today because this type of separator cannot be stored in dry condition and consequently cannot be used in so-called dry charged batteries. Moreover, some ingredients in present day batteries, which are found either in the electrolyte or in the active material, have been found to cause disintegration of cellulose material previously used as separators.

Microporous rubber separators have also been used to some extent in the battery art. Such separators, however, have been found to be relatively fragile and inflexible and, additionally, show only poor wearing resistance.

Separators consisting of cellulose fibers and impregnated with different resins have also been used, but they have poor porosity in consequence of which the internal electric resistance of a battery cell equipped with that type of separator is underrisably high.

In recent years, separators made from different suitable resinous materials have been tried. Also, many attempts have been made to use polyvinylchloride as a material for separators; however, the risk of chloride poisoning from the batteries has prevented its wide acceptance for general use. This previously used synthetic material has, however, been of a polar type material which is less desirable because of the fact that the condition of polar substances is influenced by the ion flow, which causes a change in the conductive resistance of said material. In

2

passes in one direction and in the opposite direction during discharging, in consequence of which the above said change in electric resistance arises. Suitable separators should not only have a low, but also a constant or uniform resistance in both directions.

It is therefore an object of the present invention to provide a separator and a method for production thereof, which will be of high microporosity, low and unchangeable internal resistance and yet contains pores of such a smallness as to mechanically screen metallic particles from the active material of the plate of one polarity from another of opposite polarity.

Another object of the invention is to provide a separator that will have sufficient mechanical strength to maintain shape during handling and when in a wet condition.

It is a further object of the invention to provide a separator of the type described above that is highly resistant to the oxidizing condition in a storage battery.

It is a still further object of the invention to provide an improved method for the production of separators and diaphragms for electric storage batteries and also for the production of microporous sheet like material suitable for making these separators.

Further objects will be apparent to those skilled in the art from the following description and from the appended claims.

The microporous sheet material of this invention is made of a non-polar polyolefine which is treated with an inorganic salt, a swellable material, and a leaching liquid to provide the microporosity.

The non-polar compounds have straight molecule chains and are known as straight linked materials. Due to its molecular construction such material is smooth and separators made from such material have a low friction coefficient, which in turn reduces the friction between electrodes and separators. Polyethylene, polypropylene, polybutylene and other polyolefines are examples of the different kinds of non-polar materials that may be used. The inorganic salt used may be sodium sulphate, potassium sulphate, aluminum sulphate, or magnesium sulphate. The swellable material may be starch, for example, and the leaching liquid may be water or a suitable acid or lye depending on what salts and what swellable material are added to the polyolefine.

In a preferred embodiment of the present invention, a microporous sheet material is made of 5 to 35% microporous polyethylene, 45 to 85% inorganic material, and 1 to 20% starch. It is important that the amount of inorganic salt be considerably larger than the amount of organic expandable material. A specific example of the composition is as follows:

	Percent
Polyethylene	12
Sodium sulphate.....	78
Starch	10

In the first step of the process the polyethylene is pulverized and mixed with a levigated inorganic salt such as sodium sulphate. Next a small amount of starch which swells in a liquid is mixed in. In the mixture of fine particles, the amount of leachable material is smaller than the amount of the inorganic salt. Said inorganic material constitutes mainly the pore former while the advantage of said organic expandable material is that the leaching of said inorganic salt is facilitated when the material is brought into the form of a sheet and in this form has been stabilized. Consequently, the main purpose of said organic material is not to serve as a pore former in itself, but to facilitate leaching of the inorganic salt.

After the pulverized ingredients have been mixed to a flattened out

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3

shape in a so-called calendar roller mill to the desired form.

Preferably, the mix in powder form is first passed through heating rollers at which time the polyethylene is at least partially melted and sinters together, whereupon the resulting mat passes through cold rollers and there takes on its definitive thickness and stabilizes in the desired dimension.

Next, the material is exposed to a leaching process in which the organic material, starch, swells and thereby facilitates the solution of the inorganic salt in water, for example. Thereafter, the material may be dried and cut into the desired shape. If desired, the material may be treated with sulphuric acid or the like to decompose and leach the starch out before drying.

The microporous polyethylene sheet thus formed is suitable as a separator material owing to its resistance against oxidizing attacks. Further, since the material has a low friction coefficient, a thorough wearing is not to be apprehended, due to the friction between electrode plates and separators. Moreover, a separator in accordance with the present invention is flexible, has a high solidity, and its raw material costs and cost of production are low. Also characteristic of the separator is the fact that active particles that may come from the electrode plates will not stick to its surface. In that way, the porosity of said separator is not reduced, and therefore an advantageous result is obtained with respect to the internal resistance and capacity of a storage battery cell. Further, through the treatment of calendaring, an orientation of the molecule chains in the plane of the produced sheet is obtained, thereby improving the mechanical stability and friction coefficient. Sometimes it may be advantageous to undertake a pre-orientation of the molecule chains in the material by extrusion, and to use said pre-oriented materials as initial material when calendaring to sheet shape.

The leaching procedures may also be varied as appears suitable with respect to the composition of the material mixture and the salts in said mixture. Sometimes it may be advantageous to undertake the leaching procedure or a part of it during the electrolysis, at which time the sheet material passes between electrodes in a suitable electrolyte, in order to hasten the redeeming of said inorganic salt.

According to another method of production, the mixture of material of powdered or pulverized material is distributed in a layer of even thickness to a belt or the like and is brought to sinter together so that a relatively thick and a loosely joined mat is formed, which by rolling, preferably during influence of heat, is reduced to the desired thickness and is stabilized, as by cold rolling. Instead of rolling, one or more pressure procedures, as by plane plates, may be used.

The invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. The present embodiments are therefore to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than by the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

What is claimed and desired to be secured by United States Letters Patent is:

1. A method of manufacturing a microporous partition wall for use between electrodes in an electric storage battery comprising the steps of mixing a resinous polyolefine polymer material together with an inorganic salt

4

and a swellable material, subjecting said mixture to conditions sufficient to cause said inorganic salt to form pores in said polymer material, and leaching the remnants of said inorganic salt from said mixture, said salt remnants being made readily accessible to the leaching liquid by the swelling of said swellable material.

2. A method of manufacturing a microporous partition wall for use between electrodes in an electric storage battery comprising the steps of mixing resinous polyolefine polymer material together with an inorganic salt and a swellable material, treating said mixture until the resinous particles are sintered together, bringing the sintered mass into sheet form, and leaching the remnants of said inorganic salt from said mixture, the swellable material enlarging during said leaching to facilitate removal of said inorganic salt.

3. A method of manufacturing a microporous partition wall for use between electrodes in an electric storage battery comprising the steps of mixing resinous polyolefine polymer material together with an inorganic salt and a swellable material, forming said mixture into sheet form, and treating the sheet-like body in a liquid until the swellable material swells and the inorganic salt is dissolved.

4. A method of making a microporous non-polar polyolefine storage battery electrode partition wall comprising the steps of mixing an inorganic salt and a swellable material with polyolefine to form a substantially homogeneous mixture, forming said mixture into a sheet-like body, and treating said body with a leaching liquid, said inorganic salt forming pores in said polyolefine material and said swellable material swelling sufficiently to enable said salt to be removed from said mixture after said pore formation.

5. A method as defined in claim 4 wherein said swellable material is starch.

6. In a method of manufacturing a microporous material from a resinous thermoplastic polymeric material containing a dispersion of particles of an inorganic salt, the step of adding a swellable material to said plastic to enhance leaching of said inorganic salt by swelling sufficiently to render said inorganic salt readily accessible to a leaching liquid.

7. A composition of matter for use in making a microporous material causing about 5 to 35% a resinous thermoplastic polymeric material, 45 to 85% inorganic salt, and about 1 to 20% starch, said starch being added in sufficient amount to facilitate leaching of said inorganic salt from said composition of matter by swelling when exposed to a leaching liquid and thereby rendering said inorganic salt readily accessible to a leaching liquid.

8. A composition of matter for use in making a microporous sheet-like material comprising a non-polar resinous polyolefine polymer, an inorganic salt, and a swellable material capable of swelling upon contact with a solvent liquid when applied to said mixture to leach said inorganic salt from said composition of matter.

9. The composition as defined in claim 8, wherein said polyolefine is selected from the group consisting of polyethylene, polypropylene, and polybutylene.

10. The composition as defined in claim 8, in which the inorganic salt is selected from the group consisting of aluminum sulphate, sodium sulphate, potassium sulphate, and magnesium sulphate.

References Cited in the file of this patent

UNITED STATES PATENTS

2,138,712	Saffert	Nov. 29, 1938
2,676,929	Duddy	Apr. 27, 1954

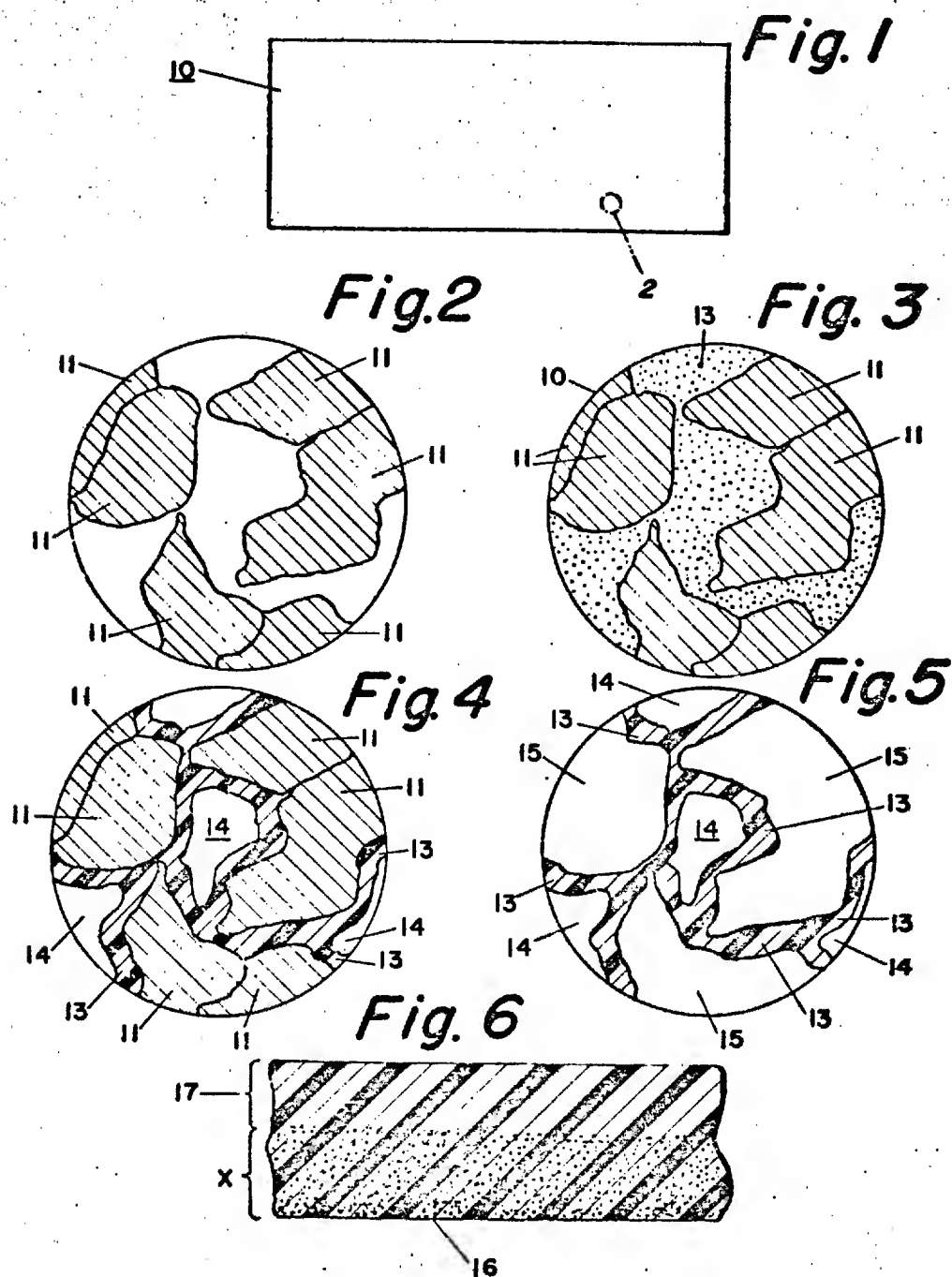
Aug. 24, 1965

H. J. STRAUSS

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METHOD OF MAKING MICROPOROUS PLASTIC

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METHOD OF MAKING MICROPOROUS PLASTIC

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13 Claims. (Cl. 264-49)

This invention relates to a method of making microporous plastics and has for an object the preparation of microporous plastics having softening points significantly higher than 300° F., such as fluorocarbon resins.

The preparation of plastics having softening points significantly higher than 300° F. has not been prepared in microporous form by an extractive process due to the difficulty of dispersing a pore-forming agent in a plastic having such an extremely high melting point. The plastics in the group generically known as fluorocarbon resins have such high melting points. Fluorocarbon resins, as well known in the art, include such plastic materials as polytetrafluoroethylene (sold commercially under the trademark Teflon) and a polychlorotrifluoroethylene (sold commercially under the trademark Kel-F) and equivalents, such as described in Modern Plastics Encyclopedia Issue for 1961 and in the book entitled "Fluorocarbons," by Rudner, published by Reinhold Publishing Corp., New York (1958).

The principal manner in which such plastic materials as Teflon TFE (polytetrafluoroethylene) or Teflon FEP (copolymer of tetrafluoroethylene and hexafluoropropylene) have heretofore been made porous is by the sintering of the particulate plastic after it has been laid down in the form of a sheet. This prior process is difficult to carry out properly, produces poor strength, non-uniform pore structure and rather large pores which are unsuitable for many purposes.

The present invention is directed to the method of producing a truly microporous form of plastic by an extractive method which enables the size of the pore structure to be accurately controlled and at the same time permits the microporous plastic to be produced in substantially any physical shape desired.

In accordance with the present invention, there is provided a method of making microporous plastic including the steps of impregnating a porous metal form with a fine dispersion of the plastic in water and drying the form to remove the water while leaving a residue of the plastic in the pores of the metal form. The plastic impregnated form is heated to a temperature and for a period of time sufficient to fuse the plastic in the pores of the metal form and the metal is thereafter removed from the plastic impregnated form by dissolution thereby producing a microporous plastic having a geometric shape corresponding to the original porous metal form and having a pore structure corresponding in volume to the metal in the original form plus the volume of the water which was removed by drying.

The method is particularly adapted for making microporous fluorocarbon resin which is particularly suited for use as electrolytic diaphragms and corrosion-resistant linings.

For a more detailed understanding of the invention and for further objects and advantages thereof, reference is to be had to the following description taken in conjunction with the accompanying drawings in which:

FIG. 1 is a diagrammatic view of a porous metal form useful in practicing the method of the present invention;

FIG. 2 is a fractional view of a portion of FIG. 1 enlarged many times to show the porous metal structure of the form in FIG. 1;

FIG. 3 is a view similar to FIG. 2 with the porous

2

metal impregnated with a fine dispersion of plastic in water;

FIG. 4 is a view similar to FIGS. 2 and 3 showing the residue of plastic in the pores of the metal form;

FIG. 5 is a view similar to FIG. 4 showing the fused microporous plastic after the removal of the metal by dissolution; and

FIG. 6 is a diagrammatic view showing a layer of microporous plastic having a layer of non-porous plastic laminated or otherwise secured to one side thereof.

In making a microporous plastic in accordance with the present invention, it is first necessary to prepare a microporous form of the desired shape and of a material which is capable of being heated to the fusion temperature of the plastic. For convenience the present invention will be described in connection with the method of producing microporous Teflon although it is to be understood that this method is applicable to other microporous plastic materials and particularly other microporous plastic materials having softening points significantly higher than 300° F. such as fluorocarbon resins.

In regard to Teflon, the fusion temperature is in the order of 750° F. and thus the microporous form 10 of FIG. 1 must be made of a material capable of being heated to at least 750° F. Several materials for the microporous form may be used, but a preferred material and one which has been used by the applicant to make microporous Teflon is a sintered plaque of carbonyl nickel. Other suitable materials for the microporous form diagrammatically illustrated as sheet 10 in FIG. 1 are a plaque of carbonyl iron and also plaques of various sintered powdered metals. Carbonyl is used because it produces plaques of very low density. Other porous metal forms may be used, such for example as porous steel, although the density of the latter is substantially higher than the density of carbonyl.

While the porous metal form 10 of FIG. 1 has been shown in the form of a sheet, it is to be understood that the porous metal form may be made in any desired shape including tubular shape. After the porous metal form 10 has been made into the desired shape, it is impregnated with an aqueous dispersion of the plastic. Such a dispersion of Teflon is available commercially under the name Teflon 30, see pages 90-96 of "Fluorocarbons" by Rudner. This is a fine dispersion of Teflon in water, i.e., very small particles of tetrafluoroethylene resin suspended in water. The dispersion is a hydrophobic, negatively charged colloid averaging about 0.5 micron in diameter. It usually contains about 59-61% by weight Teflon as solids, and is stabilized with a non-ionic wetting agent. The particle size of the Teflon is considerably smaller than the pore opening in the porous nickel plaque or form 10. It is important that this relationship of pore size be maintained when using other plastics or other porous metal forms, i.e., the particle size of the plastic must be smaller than the pore openings in the porous metal forms. To provide this relationship, the ratio of the average particle size of the metal powder to the average particle size of the plastic should be about 10 to 1 or greater. In other words, with a Teflon dispersion the particle size of the metal powder should have an average diameter of five microns or more. If a smaller ratio were used the impregnation would not be sufficiently uniform.

The microporous structure of the porous metal form 10 is shown on enlarged scale in FIG. 2. The metal particles 11 of the form have been sectioned for metal and the un-sectioned portions of FIG. 2 represent the void areas.

In FIG. 3 it will be seen that the porous metal form 10 has been impregnated with a fine dispersion of the plastic in water i.e. Teflon 30. The plastic has been indicated

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3

by the small dots 13 and in combination with the water fills the void areas between the metal particles 11. In order to more thoroughly impregnate the metal form 10 with the Teflon 30 dispersion, the impregnation is assisted by subjecting the impregnation operation to a high vacuum, for example in the order of 28" of mercury.

After the form 10 has been impregnated with the Teflon 30 dispersion, it is carefully dried so as to eliminate the water associated with the Teflon 30 dispersion thereby leaving a residue of Teflon TFE in the pores of the metal form 10. This residue is indicated at 13 in FIG. 4. The drying operation is accomplished by heating the impregnated metal form to a temperature within the range of about 100° F. to 160° F. and substantially below the boiling point of water to assure proper distribution of residues.

As will be seen in FIG. 4, the plain areas 14 represent the voids resulting from the drying operation and these voids 14 are of substantially less area than the original void areas in the porous metal form 10 illustrated in FIG. 2. After the metal form 10 has been dried leaving a porous structure including metal particles 11 and a residue of Teflon TFE as indicated in FIG. 4, the metal form 10 is then subjected to temperatures and for a period of time which will fuse the Teflon. For example, the Teflon will fuse when subjected to a temperature in the order of 750° F. for a period of about one hour. After the Teflon has been fused, the pore structure of the impregnated form 10 will continue to be similar to that shown in FIG. 4, the essential difference being that the Teflon is now in a fused state.

After the fusion step the metal form 10 will include continuous phases of metal, Teflon and air. In order to be sure to expose the metal at the surfaces, the surface of the impregnated form is prepared by light sanding such as with a fine emery paper. The next step is to remove the metal from the plastic impregnated form. This may be accomplished either by chemical or electrolytic dissolution. For example, with a nickel form, the nickel may be removed by making the form an anode in a bath of dilute sulphuric acid. A suitable electrolyte may have a strength in the order of 10% sulphuric acid. A suitable voltage across the electrodes may be in the order of two volts D.C. The electrolyte may be changed when the dissolution action slows up. Such electrolytic dissolution is preferred since no gas is produced. The nickel may also be dissolved chemically, such as in a solution of hydrochloric acid or a solution of hydrochloric acid and nitric acid, the latter being known generally by the term "aqua regia." This will dissolve the nickel in the form 10 but hydrogen is produced and remains in the pores of the form and slows down the action. Since the metal or nickel phase is continuous, it can be completely removed in the foregoing manner leaving voids 15 and 14 which together represent the volume of the metal form plus the volume of the water which was removed by the drying operation. The voids 15 produced by dissolution of the metal particles are illustrated in FIG. 5 where it will be noted that the metal particles 11 have been eliminated from the microporous form 10 and all that remains is the Teflon structure 13. In this way a "negative" image of the original pore structure of the metal plaque, FIG. 2, modified by the voids 14, produced by the evaporation of water after the original impregnation, is obtained.

The variations that are inherent in this process will permit the preparation of microporous plastic having functional temperatures in excess of 500° F. As pointed out above, the microporous plastic need not be prepared in sheet form, but rather can be prepared in any form in which porous metals can be made. The technology of making carbonyl iron plaques is such that practically any physical shape can be made and the physical form of the resultant microporous plastic will of course reflect the geometrical properties of the metal plaque or form from which it was made.

4

The present invention is particularly suited for making electrolytic diaphragms which are corrosion resistant and have the desired microporous characteristics. The pore size of the resulting microporous plastic may be controlled in various ways. In the first place, the pore size may be controlled by the pore structure of the porous metal form 10. Secondly, the pore size may be controlled by the concentration of the Teflon dispersion. For example, to provide greater voids in the end product more water is used in the dispersion. To provide smaller voids in the end product, less water is used in the dispersion. The pore size may also be controlled by the number of impregnations of the porous metal form 10: the higher the number of impregnations, the smaller the resulting pore size in the end product. Lastly, the pore size in the end product may be controlled by impregnating the form after it has been sintered so as to fill up some of the voids with inert material. Thus, the unsintered plastic or Teflon will be present as a filler when the form is impregnated after the sintering operation.

While the present invention is applicable to various uses where the entire Teflon structure is microporous, it is also applicable to uses where only one side of the structure is microporous, such as for example as in corrosion resistant linings. In this latter application, it is desirable that one side of the corrosion resistant lining be microporous so that it may be readily adhesively secured to the inside of a metal container but the opposite side or surface of the Teflon lining should be solid or non-porous so as to prevent passage of the corrosive material through the lining. A product of this type is illustrated in FIG. 6 where the porous Teflon surface is indicated at 16 whereas the non-porous Teflon surface is indicated at 17. To prepare a sheet such as illustrated in FIG. 6 the microporous portion indicated as layer X is produced in the foregoing manner described in connection with FIGS. 1-5. If a thin non-porous layer of Teflon is desired on one side of the porous layer X such thin non-porous layer may be produced by coating the one side with Teflon 30, drying the coating, and then applying a second coating, followed by subsequent drying and repeating the coating and drying operation until the desired thickness is obtained.

Where a relatively thick non-porous coating of Teflon is desired at 17, this may be obtained by laminating a solid Teflon sheet to the porous sheet X by pressing the two sheets together and heating them to the fusion temperature of Teflon. In this embodiment, the laminating step should be performed when the microporous plastic is in the form illustrated in FIG. 4, i.e., before the metal has been removed. After the sintering or fusion of the non-porous Teflon layer to the layer of Teflon and metal of FIG. 4, the laminated or fused sheet is then subjected to the step of dissolution to remove the metal either electrolytically or chemically in the manner described above.

It is to be understood that the invention is not limited to the specific arrangements shown that changes and modifications may be made within the scope of the appended claims.

What is claimed is:

1. A method of making microporous plastic having a functional temperature in excess of 500° F. comprising the steps of impregnating a porous metal form with a fine dispersion of the plastic in water, drying the form to remove the water while leaving a residue of the plastic in the pores of the metal form, heating the plastic impregnated form to a temperature and for a period of time sufficient to fuse the plastic in the pores of the metal form, and removing the metal from the plastic impregnated form by dissolution thereby producing a microporous plastic having a geometric shape corresponding to the original porous metal form and having pore structure corresponding in volume to the metal in the

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5

original metal form plus the volume of the water which was removed by drying.

2. The method according to claim 1 wherein the step of impregnating is performed under a high vacuum.

3. The method according to claim 1 wherein the metal is removed from the plastic impregnated form by chemical dissolution.

4. The method according to claim 1 wherein the metal is removed from the plastic impregnated form by electrolytic dissolution.

5. The method according to claim 1 wherein the plastic impregnated form is heated to substantially above room temperature before removing the metal.

6. A method of making microporous fluorocarbon resin having a functional temperature in excess of 500° F. comprising the steps of impregnating a porous metal form with a fine dispersion of the fluorocarbon resin in water, drying the form to remove the water while leaving a residue of the fluorocarbon resin in the pores of the metal form, heating the fluorocarbon resin impregnated form to the fusion temperature of the fluorocarbon resin and for a period of time sufficient to fuse the fluorocarbon resin in the porous and metal form, and removing the metal from the fluorocarbon resin impregnated form by dissolution thereby producing a microporous fluorocarbon resin having a geometric shape corresponding to the original porous metal form and having pore structure corresponding in volume to the metal in the original metal form plus the volume of water which was removed by drying.

7. The method according to claim 6 wherein the step of impregnating is performed under a high vacuum.

8. The method according to claim 6 wherein the porous metal form comprises a plaque of carbonyl nickel having a predetermined geometric shape.

9. The method according to claim 6 wherein the porous metal form comprises a plaque of carbonyl iron having a predetermined geometric shape.

10. A method of making a predetermined geometric shape of microporous polytetrafluoroethylene having a functional temperature in excess of 500° F. comprising the steps of impregnating a porous metal form having the desired geometric shape with a fine dispersion of the polytetrafluoroethylene in water while subjecting the impregnation step to vacuum, drying the form to remove the water while leaving a residue of the polytetrafluoroethylene in the pores of the metal form, heating the polytetrafluoroethylene impregnated form to a temperature and for a time sufficient to fuse polytetrafluoroethylene in the pores of the metal form, and removing the metal from the polytetrafluoroethylene impregnated form by dissolution thereby producing a microporous polytetrafluoroethylene having geometric shape corresponding to the porous metal form and having pore structure corresponding in volume to the metal in the original metal form plus the volume of the water which was removed by drying.

11. A method of making a microporous plastic having a functional temperature in excess of 500° F. and having

6

one side thereof non-porous comprising the steps of impregnating a porous metal form with a fine dispersion of the plastic in water, drying the form to remove the water while leaving a residue of the plastic in the pores of the metal form, heating the plastic impregnated form to a temperature and for a period of time sufficient to fuse the plastic in the pores of the metal form, removing the metal from the plastic impregnated form by dissolution thereby producing a microporous plastic having a geometric shape corresponding to the original porous form and having pore structure corresponding in volume to the metal in the original metal form plus the volume of water which was removed by drying, and thereafter coating one side of the microporous plastic with a fine dispersion of the plastic in water, drying the coated side of the microporous plastic to remove the water while leaving a residue of the plastic in the pores of the side of the microporous plastic, and repeating the last two steps of the foregoing method until the desired thickness of non-microporous plastic is obtained on the selected side of the microporous plastic.

12. A method of making a microporous plastic having a functional temperature in excess of 500° F. and having a non-porous side thereof comprising the steps of impregnating a porous metal form with a fine dispersion of the plastic in water, drying the form to remove the water while leaving a residue of the plastic in the pores of the metal form, laminating a solid sheet of plastic to one side of the plastic impregnated form by placing the solid sheet against the side of the plastic impregnated form under pressure, heating the plastic impregnated form and the laminated solid sheet of porous plastic to a temperature and for a period of time sufficient to fuse the plastic in the pores of the metal form, and removing the metal from the plastic impregnated form by dissolution thereby producing a microporous plastic having a geometric shape corresponding to the original porous form and having pore structure corresponding in volume to the metal in the original metal form plus the volume of the water which was removed by drying and one side of the microporous plastic having laminated thereto a solid non-porous sheet of the plastic material.

13. The method according to claim 1 wherein the ratio of the average particle size of the metal to that of the average particle size of the plastic is in the order of 10:1 or greater.

References Cited by the Examiner

UNITED STATES PATENTS

2,623,241	12/52	MacKay et al.	156—155 X
2,838,829	6/58	Goss et al.	117—119 X
3,009,207	11/61	Romesburg et al.	

FOREIGN PATENTS

552,914	2/58	Canada.
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United States Patent Office

3,235,409

Patented Feb. 15, 1966

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3,235,409

IRRADIATED BATTERY SEPARATOR
MEMBRANES

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No Drawing. Filed July 14, 1961, Ser. No. 123,995
2 Claims. (Cl. 136-146)

The present invention concerns ion-permeable mem-
branes that are advantageously adaptable for a variety
of uses wherein the passage of ions through a water-insol-
uble but bibulous barrier is of interest. Particularly,
the invention relates to membranes of certain water-solu-
ble mixed cellulose ether derivatives insolubilized with
high energy ionizing radiation.

In the prior art, A. A. Miller, in United States Letters
Patent No. 2,895,891, teaches how water-soluble cellulose
ethers can be cross-linked with high energy radiation
in the presence of water to provide materials useful for
fibers, tapes, fabrics, electrical insulation and the like.

It has now been discovered that certain mixed hy-
droxyalkyl methyl cellulose ethers in the form of an
aqueous sol are cross-linked with controlled amounts of
high energy ionizing radiation to provide water-insoluble,
yet bibulous, membranes that are exceptionally useful in
applications wherein ion permeability is of particular in-
terest. One such application involves the use of such
membranes in the construction of primary galvanic dry
cells. The problems encountered in this art and the
objects to be attained with improved separators for use
in battery construction are set forth by N. C. Cahoon in
United States Letters Patent No. 2,534,336.

In this reference, it is proposed to prepare separators
from membranes of water-soluble alkyl cellulose ethers
which have been either insolubilized with a polybasic
acid or coated on an inert, water-insoluble but ion-perme-
able, supporting substrate to provide a composite separa-
tor stock.

Later teachings in the art are directed to improve separa-
tors prepared from specific alkyl cellulose ethers, e.g.,
methyl cellulose ethers (United States Letters Patent No.
2,551,799) and alkali-soluble methyl cellulose ethers con-
taining from 10 to 20 percent methoxyl content (United
States Letters Patent No. 2,900,433). As will be demon-
strated in the following, the membranes of the present
invention achieve a highly surprising improvement over
other irradiated cellulose ethers and separators heretofore
taught or suggested by the prior art.

In accordance with the invention, a superior ion-
permeable, bibulous membrane is prepared by subjecting
a layer of an aqueous sol or dispersion containing from
about 1 up to about 50 percent by weight of certain hy-
droxyalkyl methyl cellulose ethers to a dose of high energy
radiation of from about 0.25 up to 5 megarads. The
wet bibulous layer thus treated can be utilized for an
ion-permeable but water-insoluble membrane as produced
or it can be subsequently dried at moderate temperatures
for more convenient handling and manipulation. Upon
rewetting, the dried hydrophilic layer can absorb several
times its weight of water to provide an ion-permeable
membrane comparable to that initially obtained upon
irradiation of the sol.

Operable cellulose ethers have a hydroxyalkyl degree of
substitution (D.S.) for each glucose residue moiety of
about 0.05 and about 0.5 and a methyl degree of sub-
stitution for each glucose residue moiety of about 0.9
to about 2. The hydroxyalkyl groups contain from 2
to 4 carbons.

If necessary, the pH of the sol is adjusted to within
the range of about 2 to about 8 prior to being irradiated.

2

The preferred pH range during irradiation is from about
3 to about 6.

Ionizing radiation that can be employed in the practice
of the present invention may range from about 50,000
up to 20,000,000 electron volts or more depending upon
the thickness of the sol layer and the concentration of
the cellulose ether therein. The dosage employed is
specified in millions of rads. A rad is defined as 100
ergs of radiation energy absorbed per gram of material
exposed. Examples of sources for such radiation are
neutrons or mixed neutron and gamma radiation such
as can be obtained in atomic reactors. Preferably, from
the standpoint of convenience of operation, the high
energy ionizing radiation source is an electron accelerat-
ing device. Ordinarily when employing high energy elec-
trons, the dosage rate is expressed as beam current amper-
age. In the practice of the invention, beam currents in
the range from 25 to 5,000 microamperes can be
employed.

Membranes of any practicable shape or thickness up
to several inches can be prepared in accordance with the
invention. The particular needs of the application for
such membranes under consideration will determine the
effective and optimum thicknesses. The actual thick-
ness of the membrane, dry or wet, will be determined
in part by the concentration of the cellulose ether in the
sol employed and the extent to which such sol is irradiated.

The layers of the aqueous sol are formed by any con-
venient means. The actual forming operation that may
be employed most effectively with any particular sol is,
to some extent, dependent upon the amount of cellulose
ether solids present in the sol. With lower amounts,
say from about 1 up to 20 percent by weight of the cellu-
lose ether, the forming of the layers to be irradiated is
effectively accomplished by casting a film on an inert sup-
porting surface of any desired shape. Sols that contain
larger amounts of the cellulose ether solids are sufficiently
viscous or thick that they can be extruded to provide a
layer in any continuous shape. When employed as
battery separators, the membranes should have, for effective
operation, a uniform thickness in the dry state within
the range from about 1 up to 4 mils.

While the irradiated membranes of the invention are
usually employed as the sole component of the battery
separator, it is possible to prepare such membranes on
an ion-permeable, water-insoluble support backing. For
example, a two component separator is prepared by cal-
endering or coating a thin paper support with the aqueous
sol as described above and thereafter subjecting the coated
support to high energy radiation in the manner that the
sol alone would be irradiated.

In a representative operation illustrative of the inven-
tion, a water dispersion containing 7 percent by weight
of a hydroxypropyl methyl cellulose ether having a
methoxyl degree of substitution within the range from
1.68 to 1.82 and a hydroxypropyl degree of substitution
within the range from 0.17 to 0.3 was prepared with the
conventional hot and cold water technique. The dry
cellulose ether powder was first mixed with about 0.2
of the required amount of water at a temperature of
about 85° C. and after thus wetting the powder, the re-
mainder of the required water was added as cold water.
The pH of the sol was adjusted to 5.0 with a small amount
of hydrochloric acid. The aqueous sol was then centri-
fuged in order to remove any air bubbles and the result-
ing clear sol was cast into a 35 mil layer on a flat stain-
less steel plate. This layer was irradiated with a 2 mev.
(million electron-volt) electron beam supplied from a
Van de Graaff accelerator having a total power capacity
of 0.5 kilowatt. The beam current employed was 225
microamperes and the total dose applied was 1.5 megarads.

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Subsequently, the irradiated layer was dried under ambient room conditions and removed from the stainless steel plate. The dry membrane thus prepared was 1.5 mils thick.

A second membrane was prepared in an identical manner except that the radiation dose utilized was 3.0 megarads.

The above-prepared bibulous membranes were cut into suitable shapes and incorporated into newly fabricated galvanic cells as separators between the electrolytic paste and soluble metallic anode. Standard zinc cans and carbon rods were employed for the anode and cathode, respectively. The electrolytic paste contained 2 parts by weight of an electrolyte and 5 parts by weight of a depolarizer mix. The electrolyte consisted of an aqueous solution containing 150 grams per liter of ammonium chloride, 90 grams per liter of zinc chloride and 0.5 gram per liter of mercuric chloride. The depolarizer mix consisted of 86 percent by weight manganese oxide, 4.2 percent by weight ammonium chloride and 9.8 percent by weight carbon black.

The assembled batteries were tested by discharging them 5 minutes per day in a circuit having an impedance of 4 ohms. Assuming a 0.75 volt cut-off point as determining the useful life of a cell, the lives of the batteries were thus ascertained. The battery that contained the separator that had been treated with 1.5 megarads had a useful life of 372 minutes. The battery having a separator of the second prepared membrane had a useful life of 325 minutes.

In other operations similar to those of the foregoing, additional batteries were prepared wherein the separators were of kraft paper and commercial battery separator paper. The useful lives of otherwise identical batteries prepared with each of the above separator membranes were ascertained in accordance with the above test procedures. Batteries prepared with the kraft and commercial battery papers had lives of 17 and 195 minutes, respectively.

Additional batteries were prepared in identical manner to that above except that the battery separator employed was a membrane obtained by irradiating a 7 percent aqueous sol of a methyl cellulose ether. A 2 percent aqueous solution of the methyl cellulose ether exhibited a viscosity of 25 centipoises at 20° C. Different radiation dosages were employed ranging from 1.25 up to 3 megarads with the thickness of the dried irradiated film varying from 1 to 2 mils. The maximum battery life achieved with the separators thus prepared was 272 minutes.

In a manner similar to that of the foregoing, other

4

hydroxyalkyl methyl cellulose ethers such as water-soluble hydroxybutyl methyl cellulose ethers and hydroxyethyl methyl cellulose ethers can be employed in place of the above hydroxypropyl methyl cellulose ethers to achieve comparable results. Likewise, similarly improved results are achieved when magnesium can anodes are substituted for the zinc cans employed above.

What is claimed is:

1. A primary galvanic dry cell comprising a soluble metallic anode, an insoluble cathode, a depolarizer mix, an electrolyte and a separator between said soluble metallic anode and said depolarizer mix, said separator being composed of a water-insoluble, bibulous membrane having a thickness from about 1 up to about 4 mils prepared by subjecting a layer of an aqueous sol having a pH within the range from about 2 to about 8 and containing from about 1 up to 50 percent by weight of a hydroxyalkyl methyl cellulose ether wherein the hydroxyalkyl group contains from 2 to 4 carbon atoms and the ether is characterized by a hydroxyalkyl degree of substitution for each glucose residue moiety from about 0.05 to about 0.5 and methyl degree of substitution for each glucose residue moiety from about 0.9 to about 2 to a dose of high energy ionizing radiation of from about 0.25 up to 5 megarads.

2. A primary galvanic dry cell comprising a soluble metallic anode, an insoluble cathode, a depolarizer mix, an electrolyte and a separator between said soluble metallic anode and said depolarizer mix, said separator being composed of a water-insoluble, bibulous, composite membrane prepared by coating an ion-permeable water-insoluble support with an aqueous sol having a pH from about 2 up to about 8 and containing from about 1 up to about 50 percent by weight of hydroxyalkyl methyl cellulose ether wherein the hydroxyalkyl groups contain from 2 to 4 carbon atoms and the ether is characterized by a hydroxyalkyl degree of substitution for each glucose residue moiety of about 0.05 to about 0.5 and a methyl degree of substitution for each glucose residue moiety of about 0.9 to about 2, and thereafter subjecting the composite to a dose of high energy ionizing radiation of from about 0.25 up to about 5 megarads.

References Cited by the Examiner

UNITED STATES PATENTS

2,882,331	4/1959	Zenczak	136—146
2,895,891	7/1959	Miller	204—154
2,942,057	6/1960	Huber et al.	136—146

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3,427,206

SEPARATOR FOR ALKALINE CELLS

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 U.S. Cl. 136-146 15 Claims
 Int. Cl. H01m 3/02

ABSTRACT OF THE DISCLOSURE

A separator for secondary alkaline cells comprising a thin sheet of a graft copolymer of a polyethylene base and a graft of a polymer of an ethylenically unsaturated carboxylic acid, such as an acrylic acid. The polyethylene may first be crosslinked by irradiation and then immersed in a solution of an acrylic acid and subjected to further irradiation to form the graft copolymer.

This invention relates to secondary alkaline cells and more particularly to separators for the same.

The secondary alkaline battery systems, nickel-cadmium, silver-cadmium, and silver-zinc offer several advantages over lead acid cells. One advantage is the ability to deliver a greater amount of energy for a given weight. This advantage is particularly characteristic of the silver-cadmium and silver-zinc cells. The nickel-cadmium cells are superior to lead acid cells in their ability to deliver a high discharge current. Thus alkaline secondary battery systems are extremely attractive for various commercial, military, and aerospace applications in portable, powered appliances of all types.

Silver-cadmium and silver-zinc cells suffer from the disadvantage of limited cycle life. This disadvantage has limited their usefulness in spite of their advantages of high energy content compared to lead acid cells as above noted. One reason for the limited cycle life of silver-cadmium and silver-zinc cells is the slight, but by no means insignificant, solubility of silver oxides in the alkaline electrolyte, which customarily is 30 to 45% KOH. These oxides are present in both true solution and in colloidal solution. Transmigration of silver oxides to the negative electrode results in local couples and self-discharge of the negative plate.

Cycle life in the silver-zinc system is further impaired by the high solubility of zinc oxide as potassium zincate. Zinc dendrites are deposited on the negative plate during charge, as a result of the reduction of zincate in solution to metallic zinc. These dendrites rapidly span the narrow gap between the positive and negative plates and short circuit the cell.

Presently known separators are unsatisfactory for alkaline cells and particularly those having silver electrodes. Battery engineers have sought suitable new separator materials.

Ideally, battery separators for cells having silver electrodes should be absorptive, readily allow passage of electrolyte ions so as to possess a low electrical resistance, not be adversely affected by concentrated potassium hydroxide solutions, be stable over the temperature range of -40° F. to 200° F., be impermeable to dissolved silver oxides and zincate ion and be inert to oxidation by silver oxide, silver peroxide and nascent oxygen.

The usual porous mats and so-called micro-porous materials, such as are used in the lead acid system, do not significantly prolong the lives of these cells, as these separators have too open a structure. They do not impede the passage of zincate ions or colloidal particles, nor slow the growth of zinc dendrites.

For many years, the only suitable separator membranes available were cellulose such as cellophane and supported and unsupported sausage casings, which are a purer form of regenerated cellulose.

The cellulose absorb sufficient electrolyte so as to have low electrical resistances. Furthermore, they slow the advance of silver oxides toward the negative plate by virtue of their reactivity towards silver oxides. That is, they are oxidized by the silver oxides, which in turn are reduced to silver metal which is deposited within and on the cellulosic separator. Furthermore, their swollen, gel-like state, which they possess when immersed in alkaline electrolytes, tends to retard the growth of zinc dendrites in silver-zinc cells.

The cellulose have several inherent disadvantages. They are, first of all, subject to hydrolytic attack by the electrolyte and undergo oxidative degradation in alkaline media. This attack most likely takes place by a mechanism whereby cleavage occurs at the gem-diol positions of the rings. Thus they are not notably long-lived, especially at elevated temperatures such as occur on high rate charge and discharge.

Secondly, the mechanism whereby cellulosic membranes slow the advance of silver oxides, not only somewhat reduces the available silver capacity, but, more important, so heavily loads the membrane with metallic silver that it becomes electrically conductive. Since the electrode assemblies are tightly packed, these electrically conductive silver-loaded membranes offer a path to short circuit the cell. Multiple layers of cellulose have been used to compensate for their instability and for their tendency to "load" with silver to the point of becoming electrically conductive. The loading of the cellulose membranes with silver in effect advances the silver electrode towards the growing zinc dendrites, resulting in premature shorting of the cell in spite of the multiple layers of separator material.

The penalty paid for the use of thick, multilayer systems having a thickness of 15 to 25 mils (.015 to .025 inch) or more, is a considerable reduction in the available energy and current density of the system as compared to that which is theoretically possible.

A major improvement in separators has been made by the use of conductive membranes prepared by introducing permanently bonded ionizable groups into inert polymer films. For example, the introduction of carboxyl groups into a polyethylene base polymer yields an ionically conductive membrane inert to both hydrolysis and oxidation attack in the electrolyte. It has been found that in order to obtain low electrical resistance, high concentrations of carboxyl groups are needed.

Radiation produced graft copolymers in thin sheet form, containing an ethylenically unsaturated carboxylic acid grafted to a polyolefin film, are outstanding separator materials according to his invention. Polyethylene is a preferred polyolefin, and acrylic and methacrylic acids are preferred ethylenically unsaturated acids. These copolymers have low electrical resistance. These membranes are ionically conductive and inert to hydrolysis and oxidative attack in the electrolyte. Moreover, they can be made very thin, 1 to 1.5 mils wet thickness, as compared to 4 to 6 mils wet thickness for the better cellulosic membranes. They slow the advance of dissolved silver oxides toward the negative electrode without being oxidized and without reducing the silver oxides to metallic silver. Furthermore, they are capable of being heated at 125° C. (about 250° F.) in 40% potassium hydroxide for 16 hours without deteriorating.

The rate of diffusion of dissolved silver oxides and zincate ions and the penetrability by zinc dendrites varies in graft copolymer separators as a function of the degree of crystallinity, of

3,427,206

3

the polyolefin starting material. Since grafting occurs only in the amorphous regions, the more crystalline polyethylene starting materials yield membranes with fewer and smaller pores. This has been demonstrated in permeability studies and cell testing.

Prior to this invention it was thought that membranes with low graft levels would have higher resistance but would have a greater cycle life than high graft level membranes, due to the decreased permeability to silver oxides and zinc ions in the low graft membranes.

It has been found unexpectedly according to the present invention that high graft membranes prepared from radiation cross linked polyethylene are vastly superior to other graft copolymer membranes. This unexpected superiority has been demonstrated in comparative tests of high and low graft level membranes under identical test conditions.

Cells according to the present invention are of the secondary alkaline type, containing a positive electrode, a negative electrode, an alkaline electrolyte, and a separator between the adjacent electrodes of opposite polarity. The positive electrode may be of a known electrode material such as silver or nickel and the negative electrode likewise of a known electrode material such as zinc or cadmium. Thus, silver-zinc, silver-cadmium, nickel-cadmium and nickel-zinc alkaline cells are within the purview of this invention. Each electrode may contain a single plate or a plurality of plates as is known in the art. Conventional alkaline electrolytes, such as 30 to 45% aqueous potassium hydroxide, may be used.

The novel separator materials according to the present invention are graft copolymers in which the base is a film of a polyolefin and the graft is a polymer of an ethylenically unsaturated carboxylic acid. Polyethylene is a preferred base material; blends of polyethylene with other olefinic polymers, as for example a polyethylene-polyisobutylene blend are also suitable. For best results the polyethylene should be cross linked. Cross linking is most readily achieved by exposure to a radiation source such as the beam of an electron accelerator until the total dose is at least 10 megarads. The total dose is generally in the range of 10 to 70 megarads. It is seldom necessary or desirable to irradiate to doses higher than 70 megarads. Other means for cross linking which will give an equivalent amount of cross linking are also suitable. For example, polyethylene may be cross linked with known cross linking agents such as divinyl benzene if desired. Cross linking of the polyethylene base is preferably carried out prior to grafting.

The graft polymer is preferably polyacrylic acid, polymethacrylic acid, or a copolymer of acrylic acid and methacrylic acid. Polymers of other ethylenically unsaturated carboxylic acids are also suitable however. The graft may be prepared by immersing the base film of polyethylene or other polyolefin in a solution of monomer, e.g. acrylic acid, methacrylic acid, or mixtures thereof. The solvent is preferably a liquid aliphatic or aromatic hydrocarbon, such as hexane, heptane, benzene, toluene or xylene. A small amount of a chlorinated hydrocarbon polymerization promoter such as carbon tetrachloride is also present in the monomer solution. The monomer solution with base film immersed is then exposed to polymerization conditions. Polymerization is preferably carried out by exposure of the monomer solution to a radiation source, such as cobalt-60. The total radiation dose is sufficient to effect polymerization and ordinarily is at least 1 megarad. The amount of graft is generally 5 to 15 mole percent, in which the molecular weight of the graft material is based on the molecular weight of the monomer and the molecular weight of the base material used for the calculation is the formula weight of a methylene unit.

Battery separators according to this invention are prepared in thicknesses ranging from about 0.25 to about

4

to about 1.5 mils. A preferred polyethylene base film will have a thickness of about 1.0 mil.

The total separator thickness in cells of this invention is preferably about 0.25 to about 9.0 mils. One or more layers of membrane may be used in order to achieve this thickness. Excellent results have been obtained for example with two layers of membrane according to this invention having a total separator thickness of 3 mils when compressed, i.e., a thickness of 1.5 mils per layer.

This invention will now be described with reference to specific embodiments thereof as illustrated in the examples which follow:

Example 1

A battery separator membrane is prepared from 1.0 mil, 0.914 density polyethylene film as follows: The polyethylene film is cross linked by irradiation under the beam of an electron accelerator to a total dose of 10 megarads. The cross linked film is rolled up with a cheesecloth spacer and immersed in a solution consisting of 25% glacial acrylic acid, 7.5% CCl_4 and 67.5% benzene (all solution percentages by volume). The film-solution combination is then irradiated to a total dose of 1.012 megarads at a dose rate of 50,600 rads/hour using a cobalt-60 radiation source. The film is then washed free of homopolymer. This gives a graft copolymer of a polyethylene base and a polyacrylic acid graft, the graft constituting 5.0 mole percent of the total.

Example 2

A battery separator is prepared from 1.0 mil, 0.922 density polyethylene film as follows: The film is cross linked by irradiation under the beam of an electron accelerator to a total dose of 30 megarads. The film is then rolled up with an absorbent interlayer and the roll immersed in a monomer solution consisting of 30% by volume glacial acrylic acid, 67% by volume benzene, toluene or xylene and 3% by volume carbon tetrachloride. The film-solution combination is then irradiated to a dose of 2.23 megarads at a dose rate of 17,200 rads/hour using a cobalt-60 radiation source. The membrane is washed free of homopolymer. This gives a graft copolymer in which the polyacrylic acid graft constitutes 5.4 mole percent of the total.

Example 3

A battery separator is prepared from 0.9 mil, 0.960 density polyethylene film as follows: The film is cross linked by irradiation under the beam of an electron accelerator to a total dose of 30 megarads. The cross linked film is then rolled up in absorbent paper and immersed in a solution consisting of 30% by volume glacial methacrylic acid and 70% benzene. The film-solution combination is then irradiated to a total dose of 2.7 megarads at a dose rate of 17,800 rads/hour using a cobalt-60 radiation source. The membrane is washed free of homopolymer. This gives a graft copolymer of a polyethylene base and polyacrylic acid graft, the graft constituting 7.1 mole percent of the total.

Example 4

A battery separator is prepared from 0.9 mil, 0.960 density polyethylene film having a melt index of 5.0 as follows: The film is cross linked by irradiation under the beam of an electron accelerator to a total dose of 30 megarads. The film is then rolled up in absorbent paper and immersed in a solution consisting of 25% by volume glacial acrylic acid, 70% by volume benzene and 5% by volume carbon tetrachloride. The film-solution combination is then irradiated at a dose rate of 22,300 rads/hour to a total dose of 3.35 megarads. The membrane is washed free of homopolymer. This gives a graft copolymer of polyethylene base and polyacrylic acid graft, the

3,427,206

5

Example 5

A battery separator is prepared from 1.0 mil, 0.917 density polyethylene film as follows: The film is cross linked by irradiation under the beam of an electron accelerator to a total dose of 70 megarads. The film is rolled up with an interlayer of absorbent paper and immersed in a solution consisting of 25% glacial acrylic acid, 70% benzene, and 5% carbon tetrachloride (all percentages by volume). The film-solution combination is irradiated at a dose rate of 14,500 rads/hour to a total dose of 1.044 megarads using a cobalt-60 radiation source. The film is washed free of homopolymer. The graft copolymer is then subjected to a second grafting under the same conditions as described in this example. This gives a graft copolymer in which the graft constitutes 10.1 mole percent of the total.

Example 6

A battery separator is prepared from 1.0 mil, 0.960 density, 0.2 melt index polyethylene film as follows: The film is cross linked by irradiation under the beam of an electron accelerator to a total dose of 50 megarads. The film is then rolled up with a cheesecloth spacer and immersed in a solution consisting of 25% by volume glacial acrylic acid and 75% by volume benzene. The film-solution combination is irradiated to a total dose of 1.73 megarads at a dose rate of 14,500 rads/hour using a cobalt-60 radiation source. The film is washed free of homopolymer and the grafting step as described above is repeated. This gives a graft copolymer containing 5.8 mole percent of a polyacrylic acid graft.

Example 7

A battery separator is prepared from 1.0 mil, 0.922 density polyethylene film as follows: The film is rolled up with an absorbent spacer. The roll is immersed in a solution containing 25% glacial acrylic acid, 70% toluene, and 5% carbon tetrachloride (all percentages by volume). The film-solution combination is irradiated to a total dose of 1.6 megarads at a dose rate of 16,000 rads/hour using a cobalt-60 radiation source. The membrane is washed free of homopolymer. The polyethylene is then cross linked by irradiation of the membrane under the beam of an electron accelerator to a dose of 30 megarads. This gives a graft copolymer containing 7.3 mole percent of graft.

Example 8

A battery separator is prepared from 1.0 mil, 0.917 density polyethylene as follows: The polyethylene film is cross linked with divinyl benzene. This is accomplished by immersing a film in a 5% solution of divinyl benzene in benzene and irradiating the combination of film and solution at a dose rate of 13,100 rads/hour to a total dose of 0.223 megarad. After rinsing in benzene, the cross linked film is rolled up with an absorbent interlayer and immersed in a solution consisting of 1 part glacial acrylic acid and 3 parts benzene by volume. The film-solution combination is irradiated at a dose rate of 13,100 rads/hour to a total dose of 1.71 megarads. This gives a graft copolymer containing 14.8 mole percent of polyacrylic acid graft.

Example 9

A battery separator is prepared from a 1.0 mil film extruded from a 0.938 density polyolefin resin consisting of a blend of polyisobutylene polyethylene as follows: The polyolefin film is rolled up with an absorbent spacer. The roll is immersed in a solution consisting of 1 part glacial acrylic acid, 2.8 parts of benzene and 0.2 part of a 50% divinyl benzene solution. The film-solution combination is irradiated to a dose of 2.256 megarads at a dose rate of 18,800 rads/hour using a cobalt-60 source. The copolymer contains 6.2 mole percent grafted acrylic acid. Battery separators according to this invention were in-

6

corporated in test cells and tested as described in Examples 10 and 11 which follow.

Example 10

Test cells having three plates and a capacity of two ampere hours each were constructed using the various separators indicated below. Three cells of each of the indicated separator materials were constructed. All cells were silver oxide-zinc cells having an alkaline electrolyte. Each cell had two layers of separator membrane having a total separator thickness of 3.0 mils. All cells were put on a cycle life test using a cycle of 35 minutes discharge and 85 minutes charge. Separator materials and the number of cycles to failure are indicated in Table I below.

TABLE I

Separator:	Cycles to failure (average values for 3 cells)
Low density, uncrosslinked	
7.8 mole percent graft (high graft) -----	174
Low density, uncrosslinked	
5.4 mole percent graft (low graft) -----	279
High density, uncrosslinked	
11.9 mole percent graft (high graft level) ----	532
High density crosslinked,	
30 mrads high graft level -----	249
Low density crosslinked,	
30 mrads high graft level -----	508

Example 11

A number of 25 ampere hour silver-zinc cells having an alkaline electrolyte and various separator materials as indicated in Table II below were built. All were tested on the same test cycle of 35 minutes discharge and 85 minutes charge, discharging to a 25% depth of discharge. Each cell had four layers of separator membrane, with a total separator thickness of 6.0 mils. Results showing the number of cycles to failure are indicated in Table II.

TABLE II

Separator:	Cycles to failure
High density, uncross-linked 12.2 mole percent graft -----	414 average.
Low density, cross-linked (30 mrad) 10 mole percent graft --	580 average.
Low density, cross-linked 13 mole percent graft -----	2130 average (still cycling).

We claim:

1. A secondary alkaline cell comprising a positive electrode, a negative electrode, an aqueous alkaline electrolyte, and a separator between said electrodes, said separator comprising a thin sheet of graft copolymer of a polyethylene base and a graft of a polymer of an ethylenically unsaturated carboxylic acid wherein said graft is 5-15 mole percent of said polyethylene.

2. A secondary alkaline cell comprising a positive electrode, a negative electrode, an aqueous alkaline electrolyte, and a separator between said electrodes, said separator comprising a thin sheet of a graft copolymer of a polyethylene base and a graft selected from the group consisting of polyacrylic acid, polymethacrylic acid, and acrylic acid-methacrylic acid copolymers wherein said graft is 5-15 mole percent of said polyethylene.

3. A secondary alkaline cell comprising a positive electrode, a negative electrode, an aqueous alkaline electrolyte, and a separator between said electrodes, said separator comprising a thin sheet of a graft copolymer of a base of crosslinked polyethylene and a graft selected from the group consisting of polyacrylic acid, polymethacrylic acid, and acrylic acid-methacrylic acid copolymers.

4. A secondary alkaline cell comprising a positive electrode, a negative electrode, an aqueous alkaline electro-

3,427,206

7

lyte, and a separator between said electrodes, said separator comprising a thin sheet of a graft copolymer of a base of radiation cross linked polyethylene and a graft selected from the group consisting of polyacrylic acid, polymethacrylic acid, and acrylic acid-methacrylic acid copolymers.

5 5. A secondary alkaline cell comprising a positive electrode, a negative electrode, an aqueous alkaline electrolyte, and a separator between said electrodes, said separator comprising a thin sheet of a graft copolymer of a base of polyethylene cross linked by exposure to a radiation dose of at least 10 megarads and a graft selected from the group consisting of polyacrylic acid, polymethacrylic acid, and acrylic acid-methacrylic acid copolymers.

10 6. A secondary alkaline cell comprising a positive electrode, a negative electrode, an aqueous alkaline electrolyte, and a separator between said electrodes, said separator comprising a thin sheet of a graft copolymer of a base of a polyethylene-polyisobutylene blend and a graft selected from the group consisting of polyacrylic acid, polymethacrylic acid, and acrylic acid-methacrylic acid copolymers.

15 7. A secondary alkaline cell comprising a positive electrode, a negative electrode, an aqueous alkaline electrolyte, and a separator between said electrodes, said separator having a total thickness of 0.25 to 9.0 mils and comprising at least one thin sheet of a graft copolymer of a polyolefin base and a graft selected from the group consisting of polyacrylic acid, polymethacrylic acid, and acrylic acid-methacrylic acid copolymers.

20 8. A secondary alkaline cell comprising a positive electrode, a negative electrode, an aqueous alkaline electrolyte, and a separator between said electrodes, said separator comprising a plurality of thin sheets of a graft copolymer of a polyolefin base and a graft selected from the group consisting of polyacrylic acid, polymethacrylic acid, and acrylic acid-methacrylic acid copolymers, each sheet having a thickness of 0.25 to 2.0 mils.

9. The cell of claim 5 wherein said graft is formed by

8

irradiation of said polyethylene in an organic solution of monomers of said acids, and said graft is 5-15 mole percent of said polyethylene.

10. The cell of claim 5 wherein said separator has a thickness of about 0.25 to about 2 mils.

11. The cell of claim 5 wherein said polyethylene is crosslinked by exposure to a radiation dose of at least 30 megarads.

12. The secondary alkaline cell of claim 5 wherein said graft copolymer is a radiation graft of said polyethylene in a solution of monomers of said acids.

13. The secondary alkaline cell of claim 12 wherein said radiation graft is of a dose rate of from about 13,100 to about 50,000 rads per hour to provide a total dose of at least about 1 megarad.

14. The secondary alkaline cell of claim 5 wherein said graft copolymer is polyethylene irradiated in an organic solution of monomers of said acids and wherein said base is polyethylene subsequently cross linked by said exposure to said radiation dose.

15. The secondary alkaline cell of claim 14 wherein said base is polyethylene cross linked by said exposure to a radiation dose of at least 10 megarads and said irradiation of said graft is of a lower dose than 10 megarads.

References Cited

UNITED STATES PATENTS

2,965,697	12/1960	Duddy	136-146
3,101,276	8/1963	Hendricks	117-56
3,111,424	11/1963	Le Clair	117-93.31 X
3,188,165	6/1965	Magat et al.	117-93.31 X
3,240,723	3/1966	Friedländer	136-146 X

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117-93.31

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BATTERY HAVING A POROUS INSOLUBLE HYDROUS
INORGANIC OXIDE SEPARATOR
Filed June 30, 1964

3,489,610

Fig. 1

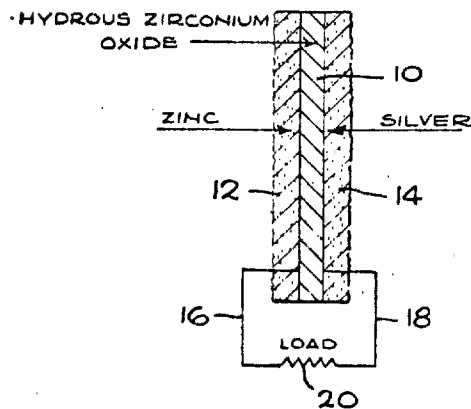


Fig. 2

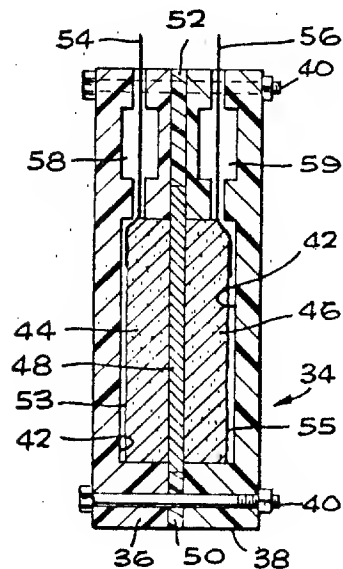
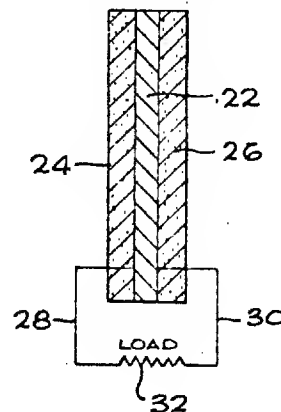


Fig. 3

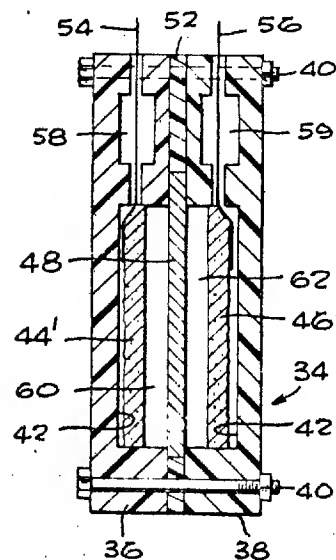


Fig. 4

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1

3,489,610

**BATTERY HAVING A POROUS INSOLUBLE
 HYDROUS INORGANIC OXIDE SEPARATOR**

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Filed June 30, 1964, Ser. No. 379,093

Int. Cl. H01m 3/02

U.S. Cl. 136—6

14 Claims 10

This invention relates to batteries, particularly high energy density batteries, and is especially concerned with the provision of improved inorganic membranes or separators for use in batteries, and to improved battery construction embodying efficient inorganic separators having a porous internal structure and pore size characteristics preventing transfer of electrode ions such as zinc and silver ions through the separator.

Batteries are an important source of energy storage for power generation in air-borne systems. An important type of battery particularly suited for such applications are the high energy density alkaline electrolyte cells using such electrode combinations as silver-zinc, silver-cadmium and nickel-cadmium. High energy density batteries are generally battery systems which have a substantially higher energy per unit of weight than conventional, e.g., lead, storage batteries. Thus, high energy density batteries can develop, e.g., 100 to 140 watt hours of energy per pound. In addition to important air-borne applications, such high energy density batteries have many other applications such as in portable tools and appliances, television, radio and record players, engine starting, portable X-ray units and the like. However, batteries in use at the present time have not given sufficiently long life, nor have they been able to operate at the extremes of high and low temperatures.

In high energy density batteries such as silver-zinc, nickel-cadmium, silver-cadmium, the separator performs the function of retaining electrolyte, e.g., potassium hydroxide, separating the electrodes, and preventing migration of electrode ions or growth of dendritic crystals of electrode ions which short circuit the battery. It has been known to employ organic separators in such batteries but these have several disadvantages. Thus, such organic separators are not chemically stable especially at temperatures above 50° C., they tend to swell excessively at elevated temperatures and most organics are not readily wetted by caustic solutions. Further, organics are not inert to silver oxide in caustic solutions and organic materials are generally soft and pliable and are subject to puncture by dendrite growth.

Some of the principal objectives in battery development and also objects of the present invention, are to obtain a higher energy per unit weight, permit operation in a higher thermal environment, and increase the life of a battery both in stand-by and discharge-recharge cycling.

It is another object of this invention to provide improved high energy density batteries having extended periods of life and which are capable of operation at high temperatures of the order of about 100° C. and above, and to provide improved inorganic battery separators especially designed for use in such batteries.

Another object of the invention is the development of inorganic battery separators and improved battery constructions, particularly for silver-zinc, silver-cadmium, nickel-cadmium, and other high energy density battery systems, for operation at temperatures from ambient up to 100° to 200° C.

2

A further object of the invention is the design of a battery particularly suited for air-borne applications, of small weight, capable of being charged and discharged over a large number of cycles, and operating particularly at elevated temperatures, said batteries being capable of withstanding temperatures of the order of 100° C. and higher, and which can take advantage of increased electrochemical activity and decreased electrolyte resistance at such elevated temperatures.

A still further object is the design of batteries and inorganic battery separators which are chemically inert particularly at elevated temperatures, are geometrically stable, readily wetted by electrolyte, are not attacked by silver oxide, can be made with controlled porosity, and which resist puncture by dendritic growth.

A still further object is the provision of improved high energy density batteries, particularly silver-zinc cells, incorporating inorganic separators which are strong, rigid and capable of supporting electrodes of opposite polarity, yet having a porosity sufficient to permit transfer of hydroxyl ions through the separator but preventing penetration of the electrode ions into and through the separator.

Other objects and advantages will appear hereinafter.

The present invention is based on the discovery that inorganic separators, particularly porous separators or membranes, and preferably composed of insoluble hydrous inorganic or metal oxides such as hydrous zirconium oxides, have many advantages over the use of organic separators, in high energy density batteries. Thus, the inorganic separators of the invention are chemically inert at all operating temperatures and particularly at elevated temperatures, e.g., above 100° C. The porosity of such inorganic separators is easily controlled and can be varied to control resistance and diffusion of ions through the separator. Such separators have geometric stability, are readily wetted by alkaline electrolytes, and are not chemically attacked by silver oxide. Further, the rigid microporous structure of such inorganic separators does not allow dendrite growth through the separator.

It is a particular feature of the inorganic separators according to the invention that although such separators can be formed into thin, strong, rigid membranes, satisfactory porosity can be provided in such hydrous metal oxide separators by various procedures of formation described below, such that the separators permit and facilitate transfer of electrolyte ions through the separator, but prevent transfer of electrode ions such as silver and zinc ions through the separator so that no treeing of, for example, zinc dendrites can occur in the separator. Thus, maximum porosity should be about 40%, and minimum porosity about 5%, and hence the separators of the invention have a porosity in the range from about 5% to about 40%. Generally, porosity of the hydrous metal oxide separator of the invention can range from about 8% to about 40%, preferably from about 10% to about 25%, as measured by water absorption according to the expression:

$$\frac{\text{Weight after water saturation} - \text{dry weight}}{\text{dry weight}} \times 100$$

The inorganic separators according to the invention are quite thin, and can have a thickness, e.g., in the range of about .005 to about 0.050 inch.

If the porosity of the separators is greater than about 40%, the strength of the separators is reduced dangerously to a point where the separator is easily broken or shattered, especially during assembly of the battery, and is incapable of properly supporting the electrodes, and too porous to prevent electrode ion passage, and if the porosity is below about 5%, the effectiveness of the battery is materially and undesirably reduced due to the substantially reduced amount of electrolyte which can be re-

tained by the separator, thereby preventing required diffusion of electrolyte ions.

A high energy density battery is accordingly provided according to the invention embodying an insoluble hydrous metal oxide separator generally having the porosity characteristics above indicated, in combination with electrodes of opposite polarity, e.g., zinc and silver electrodes, preferably in supported relation adjacent opposite sides of the separator. Such relatively rigid inorganic separator provides support for the electrodes even though the separator is very thin and has porous characteristics, as described above. These batteries, in addition to having long cycle life at elevated temperatures, have exhibited excellent charging efficiency under severe operating conditions.

By the terms "porous membrane" and "porous separator" employed herein, is intended to denote a membrane-thin plate, latticework, network or matrix having an inner structure of interconnecting micropores between its opposing surfaces.

The insoluble porous hydrous metal oxide membranes have properties and are particularly adapted to use in fuel cells and batteries where extremely strong membranes are required to maintain electrode ion separation between the electrodes of the battery or fuel cell, and wherein operating temperatures may approach and exceed 150° C. Moreover, the present invention has the distinct advantage of allowing membranes to be stored in an inert form for indefinite periods of time without change and to be employed as high strength porous membranes or separators for batteries as needed.

For the purposes of this invention, the term "insoluble hydrous metal oxides" includes those water insoluble materials containing one or more metal atoms, oxygen atoms, and an indeterminate quantity of water. The hydrous metal oxides do not necessarily have a definite stoichiometric combination or definite crystal structure and may contain ionic impurities. The water insoluble hydrous metal oxides which can be employed to form the separators of the invention are the water insoluble hydrous oxides of metals selected from the following groups of metals in the Periodic Table: III-A, III-B, IV-A, IV-B, V-A, V-B, VI-B, VII-B, VIII, the Lanthanide Series and the Actinide Series. The elements or metals forming insoluble hydrous oxides which are of greatest practical importance at the present time are: Al (III), Ga (III), In (III), Sc (III), Y (III), Zr (IV), Ti (IV), Hf (IV), Pb (II), Si (IV), Ge (IV), Sn (IV), Sb (III, V), Bi (III), As (V), V (V), Nb (V), Ta (V), Cr (III), Mo (IV, VI), W (IV, VI), Mn (IV), Re (IV), Tc (IV), Fe (III), Co (II), Ni (II), Ac (III), Th (III), U (IV, VI), Pu (IV), La (III), Ce (IV), and Yb (III). Other valence states of some of these elements may also be useful.

Materials which are particularly useful for producing inorganic separators according to the invention are the hydrous oxides of zirconium, titanium, antimony, tungsten, silicon, scandium, bismuth, vanadium, aluminum and cerium. Hydrous zirconium oxide separators are especially desirable.

Battery separators according to the invention can be prepared by various techniques. Thus, for example a separator can be prepared by (1) conversion of acid salts to the corresponding hydrous oxides, as described in the copending application Ser. No. 326,985, now Patent No. 3,346,422, filed Nov. 29, 1963, of Carl Berger, (2) flame spraying insoluble metal oxides accompanied by hydrolytic activation, as described in the copending applications Serial No. 327,114, now abandoned of Norman Michael and Ser. No. 327,038, now Patent No. 3,392,103, of Carl Berger, both filed Nov. 29, 1963, and (3) impregnating porous ceramics such as alumina or zirconia with a gel of an insoluble hydrous metal oxide such as hydrous zirconium oxide, as described in copending application Ser. No. 326,740, filed Nov. 29, 1963, of Carl Berger.

In method (1) noted above, an acid salt such as zir-

conium phosphate, can be treated with alkali, e.g., potassium hydroxide, to form hydrous zirconium oxide.

According to method (2) described above, metal oxide such as zirconia is flame-sprayed and the resulting anhydrous ceramic membrane is then treated with high temperature steam or with alkali, e.g., KOH, to partially rehydrate the base ceramic material to its hydrous state.

In procedure (3) noted above, a gel-filled membrane is formed by filling the pores of a strong porous thin plate, such as a ceramic plate, e.g., a flame-sprayed zirconia membrane, with insoluble hydrous metal oxide gel, e.g., a hydrous gel of zirconium oxide.

The descriptions of the above processes as described in the above copending applications are all incorporated herein by reference.

By the above-noted techniques, inorganic materials having excellent chemical resistance, good electrical resistivity and high strength can be formed into battery separators according to the invention. However, it is noteworthy that the hydrous metal oxides of which the invention separators are formed, provide less internal resistance than do sintered metal oxides, and such reduced internal resistance is a distinct advantage in producing efficient battery separators which have long cycle life, particularly for high energy density batteries. Further, the hydrous metal oxides hereof have ion exchange properties rendering such materials useful as ion exchange membranes in fuel cells.

By employing the procedures noted above, inorganic separators comprising hydrous metal oxides, particularly hydrous zirconium oxide, are readily produced and which have a controlled porosity within the ranges noted above. However, it will be understood that insoluble hydrous metal oxide membranes or separators produced by other procedures are also within the purview of the invention.

After formation of the hydrous oxide separator or membrane, electrodes are positioned on opposite surfaces or opposite sides of the separator. For this purpose the electrodes, e.g., zinc and silver electrodes, can be flame-sprayed onto opposite surfaces of the separator or the respective electrodes can be pressed against opposite surfaces of the separator. The hydrous metal oxide membrane can be impregnated with electrolyte, e.g., KOH, either before or after the electrodes are assembled on opposite sides of the separator. The entire assembly including the separator and the electrodes are then assembled or clamped together to form a battery. If desired, the entire assembly then can be encapsulated in an encapsulating resin. A variety of resins can be employed for this purpose, including epoxies, polyesters, phenolics, melamines, and silicones, epoxies being preferred. The resins are usually mixed with catalysts or hardeners, or both.

The invention will be further described in relation to ssembly according to the invention;

FIG. 1 is a schematic representation of a battery assembly according to the invention;

FIG. 2 is a schematic illustration of a modification of the battery unit of FIG. 1;

FIG. 3 shows the manner of assembly of a separator and electrodes to form a battery according to the invention; and

FIG. 4 shows a modification of the assembly of FIG. 3.

Referring to FIG. 1, an insoluble hydrous metal oxide membrane, e.g., hydrous zirconium oxide, represented by numeral 10, formed, for example, by any of the procedures noted above, is flame-sprayed as described above on opposite surfaces or sides with a zinc electrode indicated at 12, and with a silver electrode indicated at 14. Wires 16 and 18 connect the electrodes 12 and 14 respectively to a load 20.

In the modification of FIG. 2, a hydrous oxide separator 22 is provided and has pressed against opposite sides thereof a zinc electrode 24 and a silver electrode 26.

Wires 28 and 30 connect the respective electrodes 24 and 26 of opposite polarity, in series to a load 32.

In the modification of FIG. 2, the zinc and silver electrodes are prepared in any suitable manner, e.g., by forming a paste of these electrode materials as described below and pressing the paste against, and causing it to adhere to and to impregnate, the opposite surfaces of the inorganic separator of the invention.

During discharge of the batteries illustrated in FIGS. 1 and 2, as is well known, the zinc is converted to zinc oxide and the silver oxide to silver, and during charging of such batteries the silver is oxidized to silver oxide and the zinc oxide is reduced to zinc. Because of these reversible reactions, the terms "silver" and "zinc," the terms "silver" and "cadmium" and the terms "nickel" and "cadmium," referring to the metals forming the respective electrodes of such battery systems, are intended to denote either the respective metals themselves or the corresponding oxides thereof.

The pores of the separator 10 or 22 are filled with an alkaline electrolyte. It will be noted in the schematic illustrations of FIGS. 1 and 2 that the separator aids in supporting the sprayed on metal electrodes 12 and 14, or the electrodes 24 and 26 pressed against opposite surfaces of the separator. However, certain electrodes, particularly the zinc electrode, even when so supported, slump and deteriorate, causing failure of the battery after a number of charge-discharge cycles.

By further supporting the electrodes, particularly the zinc electrode to minimize or substantially eliminate the slumping or collapse of the electrode, according to the invention described in the copending application Ser. No. 378,859, filed June 29, 1964 of Carl Berger and Frank C. Arrance, cycle life of the battery is substantially increased at temperatures of the order of 100° C., and efficiency of the battery is improved.

The following are examples of practice of the invention:

EXAMPLE 1

A hydrous zirconium oxide membrane having a porosity of about 15% is prepared as described in Example XXVII of the above copending application Ser. No. 326,985, by ball milling 450 grams of hydrous ZrO_2 with 450 grams concentrated phosphoric acid for 18 hours. This material is dried for 15 hours at 160° C., granulated to -32 and +80 mesh particles, and pressed into a 2" disc 0.20" thick, at 15 tons pressure and sintered at 300° C. for 24 hours. The homogeneous zirconium phosphate membrane thus formed is treated with a 30% solution of potassium hydroxide under conditions to draw the solution into the pores of the membrane by suction, converting the membrane to a hydrous zirconium oxide membrane.

Silver electrode material is prepared using equal parts of silver oxide and silver. These materials are mixed with a high speed vibrating mixer and pressed at 5 tons to about 15 tons total load into 2 inch diameter discs about 0.100 inch thick. The pressed discs are placed between flat smooth vitreous ceramic plates and sintered for one to four hours at temperatures ranging from 250° to 600° C. After cooling to room temperature, the sintered discs are cut to size and spot welded to a fine nickel screen.

The silver electrodes are prepared for use by electrolytic oxidation or charging at room temperature in 20% to 40% KOH. After forming, the electrode is removed from the charging stand and assembled in a battery as described below.

Zinc electrodes are prepared by mixing about 90 parts zinc oxide, 7 parts HgO , and 3 parts polyvinyl alcohol in a high speed vibratory mixer. After mixing, a weighed amount of this material is placed in an electrode compartment in contact with a fine nickel screen, mixed with a small amount of 30% KOH and electrolyzed.

The separator and electrodes described above are assembled to form a battery as shown in FIG. 3, employing a plastic case 34 formed of two symmetrical, e.g., Teflon, half portions 36 and 38 which are bolted together as indicated at 40. Compartments 36 and 38 of the case have recesses 42 formed therein to receive the zinc and silver electrodes 44 and 46 respectively, prepared as described above. The inorganic separator 48 is disposed centrally between the case portions 36 and 38 so that the electrodes 44 and 46 are pressed against opposite surfaces of such separator. Teflon spacers 50 and 52 are provided about the periphery of separator 48, to form a leak-proof seal. Nickel screens 53 and 55 are embedded in electrodes 44 and 46 adjacent to the bottom of the compartment recesses 42, and silver terminal wires 54 and 56 are connected respectively to the screens 53 and 55, and are brought through the plastic electrode sections at the top of the assembly as shown. Small electrolyte reservoirs 58 and 59 are provided in the upper portion of the respective electrode compartments 36 and 38.

In the modification shown in FIG. 4, it will be noted that the zinc and silver electrodes 44' and 46' are spaced from and are not in direct contact with, the inorganic separator 48, forming captive electrolyte compartments 60 and 62 between such electrodes and separator 48, insuring a full supply of electrolyte filling the pores of the separator at all times.

Batteries of the types described above and illustrated in FIGS. 3 and 4, can be cycled for about 300 to about 500 half hour discharge and half hour charge cycles at 100° C.

However, where the electrodes are not in direct contact with the separator, as in the embodiment of FIG. 4, the battery often fails due to the slumping of the unsupported zinc electrode 44'.

If the electrodes are supported with respect to the separator, for example, if the electrodes are in direct contact with the separator, as illustrated in FIG. 3, so that the zinc electrode has less tendency to slump and break through the separator, a substantially larger number of charge and discharge cycles can be obtained. Furnishing support for the zinc electrode according to the above-noted Berger-Arrance application Ser. No. 378,859, provides improved results.

Discharge of such batteries over a period of days has resulted in current densities of 27 amperes per square foot at 1.2 volts and at ambient temperatures. Higher temperatures will improve the performance of the battery without deteriorating the hydrous zirconium oxide separator.

EXAMPLE 2

A hydrous titanium oxide membrane is prepared as described in Example XXVIII of the above copending application Ser. No. 326,985, by first dissolving 200 grams of titanium chloride in 500 cc. of water and precipitating titanium phosphate with a 1.0 M solution of phosphoric acid at a pH of 3. The precipitate is washed, dried for 24 hours at 110° C., granulated and pressed into a membrane 0.02 inch thick at 15 tons total load. The membrane is then sintered at 1,000° C. for 15 hours to form the pyrophosphate. The membrane thus formed is supported in a 10 liter autoclave containing 1 liter of water and subjected to steam at 2,300 p.s.i. and about 350° C. for 96 hours. The membrane is then treated with a 30% solution of potassium hydroxide drawn through the pores of the membrane by suction, forming a hydrous titanium oxide membrane. Such membrane has a porosity of about 12%.

This membrane is employed as a separator in the battery of Example 1 in place of the hydrous zirconium oxide separator thereof. Results similar to Example 1 are obtained.

7

EXAMPLE 3

A hydrous zirconium oxide membrane having a thickness of about 0.020 inch and a porosity of about 15% is obtained, as described in Example V of the above copending application, Ser. No. 327,114, by treating a flame-sprayed zirconia membrane in an autoclave containing 1 liter of water. The membrane is exposed therein to steam at 1,500 p.s.i. and approximately 315° C. for 650 hours.

The resulting hydrous zirconium oxide membrane is employed as a separator in the battery unit of Example 1 herein. Results similar to Example 1 are obtained.

EXAMPLE 4

A hydrous antimony oxide membrane having a thickness of about 0.02 inch is prepared, as described in Example VI of above copending application Ser. No. 327,114, by compacting and sintering antimony oxide at 500° C. and exposing the sintered membrane in an autoclave containing water, to steam at 2,000 p.s.i. and about 340° C. for 750 hours. The membrane so formed is employed as separator in the battery unit of Example 1 above, in place of the hydrous zirconium oxide separator, obtaining results similar to those in Example 1.

EXAMPLE 5

A hydrous tungstic oxide membrane about 0.02 inch thick is prepared according to Example IX of above copending application, Ser. No. 327,038, by compacting tungstic oxide and sintering at 1,000° C. The membrane is then treated in an autoclave with 30% sodium hydroxide solution and exposed therein to steam at 2,300 p.s.i. and about 350° C. for 350 hours.

The resulting membrane is employed as separator in the battery unit of Example 1 above in place of the anhydrous zirconium oxide membrane. A battery capable of operating over a large number of discharge-charge cycles at 100° C. is obtained.

EXAMPLE 6

A battery substantially the same as that of Example 1 is fabricated except that a separator is used which is formed as described in Example XIII of above copending application, Ser. No. 326,740. Such separator is produced by treating a flame-sprayed zirconia membrane that is flooded with water in a diffusion apparatus in which the flooded membrane is a divider between the two compartments thereof, one filled with a waterglass solution and the other with a 6.0 N solution of nitric acid and diffusion of the reagents into the membrane allowed to continue for 24 hours. After removal from the diffusion apparatus the pores of the membrane are filled with a hydrous gel of silicon dioxide.

A battery as in Example 1, employing such a separator in place of the hydrous zirconium oxide separator thereof is capable of operating for over 100 discharge-charge cycles of 30 minutes each at elevated temperatures.

EXAMPLE 7

A battery substantially the same as Example 1 is fabricated except that the separator employed therein is obtained as described in Example XIV of the above copending application, Ser. No. 326,740, by flooding a flame-sprayed zirconia membrane having a porosity of about 27% with water, and employing the flooded membrane as the divider between two compartments of a diffusion apparatus, one filled with a 2.0 M zirconyl nitrate solution and the other with a 6.0 M ammonium hydroxide solution. Diffusion of the reagents into the membrane is allowed to continue for 24 hours. After removal from the diffusion apparatus, the pores of the membrane are filled with a hydrous gel of zirconium oxide.

The battery containing such flame-sprayed zirconia membrane impregnated with a hydrous gel of zirconium oxide can operate for about 300 to about 500 discharge-

8

charge cycles each of 30 minutes duration at temperature of 125° C.

EXAMPLE 8

A battery substantially similar to that of Example 1 is assembled, except that the electrodes are silver and cadmium.

Such battery can be cycled for about 1,000 to about 3,000 discharge-charge cycles at 100° C. without loss of effective capacity.

EXAMPLE 9

A battery substantially similar to that of Example 1 is assembled, except that the electrodes are nickel and cadmium.

Such a battery can be cycled for about 1,000 to about 3,000 discharge-charge cycles at 100° C. without loss of effective capacity.

EXAMPLE 10

The hydrous zirconium oxide membrane described in Example 1 above can function as an anion exchanger in a hydrazine-oxygen fuel cell.

EXAMPLE 11

A porous ceramic membrane 2" in diameter and 0.02 inch thick is prepared from scandium oxide, as described in Example II of above copending application Ser. No. 327,114, by compacting and sintering at 1,800° C. and 20 tons total load. The membrane is treated in an autoclave with water and superheated steam at 2,000 p.s.i. and about 340° C. for 750 hours, forming a hydrous scandium oxide membrane having a porosity of about 12%.

Such membrane is employed in the battery of Example 1 in place of the hydrous zirconium oxide separator thereof. Results similar to Example 1 are obtained.

EXAMPLE 12

A hydrous cerium oxide membrane having a thickness of about 0.02 inch and a porosity of about 15% is obtained as described in Example XII of the above copending application, Ser. No. 327,114 by compacting and sintering cerium oxide at 300° C. and treating the resulting membrane in an autoclave with water and steam at 2,300 p.s.i. and about 350° C. for 450 hours.

The resulting hydrous cerium oxide membrane is employed as a separator in the battery unit of Example 1 herein. Results similar to Example 1 are obtained.

EXAMPLE 13

A battery substantially the same as that of Example 1 is fabricated except that a separator is used which is formed as described in Example XVIII of above copending application Ser. No. 326,740. Such a separator is produced by flooding a flame-sprayed zirconia membrane with an aqueous solution of 1.0 M bismuth chloride containing 10% urea, and filling the pores of the membrane with the hydrous gel of bismuth oxide.

Such a battery can operate on the order of about 100 discharge-charge cycles of 30 minutes each at 100° C.

EXAMPLE 14

A battery substantially the same as that of Example 1 is fabricated except that a separator is used which is produced by impregnating the pores of a flame-sprayed zirconia membrane with a hydrous gel of vanadium oxide according to the procedure of above copending application Ser. No. 326,740.

The resulting battery can operate for a period of the order of about 100 discharge-charge cycles of 30 minutes each at 100° C.

EXAMPLE 15

A battery substantially similar to that of Example 1 is fabricated, except that in place of the separator of Example 1, a Teflon separator of substantially the same thickness is employed.

9

The Teflon is not readily wetted by the KOH electrolyte, causing the separator to have high resistance, and as a result the efficiency and capacity of the battery are substantially reduced. Such a battery runs for only about 25 discharge-charge cycles at 100° C. before battery failure occurs.

EXAMPLE 16

A hydrous zirconium oxidized membrane prepared as in Example 1 above, but having a porosity of about 3%, is employed in a battery unit as described in Example 1. This battery has a capacity of only about 5 amperes per square foot as compared to the 27 amperes per square foot of the battery of Example 1.

EXAMPLE 17

A hydrous zirconium oxide membrane is prepared as in Example 1 above, but having a porosity of about 75%. This battery runs for only about 50 to about 75 discharge-charge cycles before failing, as compared to the substantially larger number of such cycles for the battery of Example 1.

From the foregoing, it is seen that the invention provides a high energy density battery embodying hydrous metal oxide membranes or separators having porous characteristics which prevent migration of electrode ions, such as silver and zinc ions through the separator to opposite electrodes, while permitting free transfer of hydroxyl ions through the separator. Such inorganic membranes permit substantially higher temperatures of operation of the order of 100° C. and above, without deterioration of these membranes as compared to prior art, e.g., organic separators, are resistant to oxidation by electrodes, e.g., silver oxide, and are radiation resistant. Batteries incorporating the separators of the invention are capable of being cycled through many discharge-charge cycles without any substantial loss of capacity. Such separators are of rigid, relatively inflexible structure, and are capable of supporting to some degree electrodes placed on opposite sides of the separator in contact therewith.

We are aware of U.S. Patent 1,863,070. The patent describes filters or diaphragms which can be employed for electrolytic purposes, by heating or sintering of chromium oxide together with other compounds which, on being heated, decompose, leaving pores, to thereby control or increase pore size of the chromium oxide body to obtain a high porosity membrane. It is stated in the patent that other heavy metal oxides such as zirconium oxide can also be used.

The hydrous metal oxide separators of the invention have advantages for use in batteries not possessed by the sintered oxides of the patent. Thus, for example, although the insoluble hydrous oxide separators of the invention are dielectric materials and have substantial internal resistance, their resistance in this respect is not nearly as high as that of the sintered inorganic oxides such as the sintered chromium oxide and the sintered zirconium oxide diaphragms of the patent, and thus, batteries embodying the hydrous oxide separators of the invention have substantially less internal resistance and are therefore more efficient than batteries employing the sintered chromium oxide and sintered zirconium oxide diaphragms of the patent. Further, the sintered metal oxide diaphragms of the above patent have a substantially greater porosity than the hydrous oxide separators of the invention and would result in batteries of substantially reduced cycle life and of low strength.

Moreover, hydrous metal oxides employed in the separators of the invention have ion exchange characteristics, which render such separators particularly suited for use in fuel cells as well as in batteries, whereas the sintered oxide diaphragms of the patent have no ion exchange properties.

It will be understood that the hydrous metal oxide separators of the invention can be employed in con-

10

junction with any desired electrode system, including silver-zinc, silver-cadmium, nickel-cadmium, and the like.

While we have described particular embodiments of our invention for purposes of illustration, it will be understood that the invention is not to be taken as limited except by the scope of the appended claims.

We claim:

1. A battery comprising a pair of electrodes of opposite polarity and a porous separator between said electrodes for retaining electrolyte and permitting transfer of electrolyte ions, said separator consisting essentially of a porous insoluble hydrous inorganic oxide and said separator having a porosity permitting transfer of electrolyte ions through such separator, but preventing transfer of electrode ions therethrough.
2. A battery as defined in claim 1, said insoluble hydrous inorganic oxide being a porous insoluble hydrous metal oxide wherein said metallic element is selected from the group consisting of Al, Ga, In, Sc, Y, Zr, Ti, Hf, Pb, Si, Ge, Sn, Sb, Bi, As, V, Nb, Ta, Cr, Mo, W, Mn, Re, Tc, Fe, Co, Ni, Ac, Th, U, Pu, La, Ce and Yb, and said separator having a porosity in the range from about 5% to about 40%.
3. A battery comprising a pair of electrodes of opposite polarity and a porous rigid separator between said electrodes for retaining electrolyte and permitting transfer of electrolyte ions, said separator consisting essentially of a porous insoluble hydrous metal oxide and said separator having a porosity in the range from about 5% to about 40%.
4. A battery comprising a pair of electrodes of opposite polarity and a porous rigid separator between said electrodes for retaining electrolyte and permitting transfer of electrolyte ions, and an electrolyte in the pores of said separator, said electrodes being disposed in supported relation against opposite surfaces of said separator, said separator consisting essentially of a porous insoluble hydrous metal oxide and said separator having a porosity in the range from about 5% to about 40%.
5. A battery comprising a pair of electrodes of opposite polarity and a porous rigid separator between said electrodes for retaining electrolyte and permitting transfer of electrolyte ions, said separator consisting essentially of a porous insoluble hydrous metal oxide of a metal selected from the group consisting of zirconium, titanium, antimony, tungsten, silicon, scandium, bismuth, vanadium, aluminum and cerium, said hydrous oxide separator having a porosity in the range from about 5% to about 40%.
6. A battery comprising a pair of electrodes of opposite polarity and a porous separator between said electrodes for retaining electrolyte and permitting transfer of electrolyte ions, and an electrolyte in the pores of said separator, said separator being a rigid membrane consisting essentially of a porous insoluble hydrous metal oxide of a metal selected from the group consisting of zirconium, titanium, antimony, tungsten, silicon, scandium, bismuth, vanadium, aluminum and cerium, said hydrous oxide separator having a porosity in the range of about 10% to about 25%.
7. A battery comprising a pair of electrodes of opposite polarity and a porous separator between said electrodes for retaining electrolyte and permitting transfer of electrolyte ions, and an electrolyte in the pores of said separator, said separator being a rigid membrane consisting essentially of hydrous zirconium oxide and said separator having a porosity in the range from about 5% to about 40%.
8. A battery comprising a pair of electrodes of opposite polarity and a porous separator between said electrodes for retaining electrolyte and permitting transfer of electrolyte ions, said electrodes being disposed in supported relation against opposite surfaces of said separator, said separator being a rigid membrane consisting essentially of hydrous zirconium oxide and said separator having a porosity in the range from about 5% to about 40%.

11

9. A battery comprising zinc and silver electrodes and a porous rigid separator between said electrodes for retaining electrolyte and permitting transfer of electrolyte ions, said separator consisting essentially of a porous insoluble hydrous metal oxide of a metal selected from the group consisting of zirconium, titanium, antimony, tungsten, silicon, scandium, bismuth, vanadium, aluminum and cerium, said hydrous oxide separator having a porosity in the range from about 5% to about 40%.

10. A battery comprising zinc and silver electrodes and a porous separator between said electrodes for retaining electrolyte and permitting transfer of electrolyte ions, and an electrolyte in the pores of said separator, said separator being a strong rigid membrane consisting essentially of hydrous zirconium oxide and said separator having a porosity in the range from about 5% to about 40%.

11. A battery as defined in claim 10, wherein the porosity of said membrane ranges from about 10% to about 25%.

12. A battery comprising a pair of electrodes of opposite polarity and a porous separator between said electrodes for retaining electrolyte and permitting transfer of electrolyte ions, said separator being composed of a porous thin rigid inert plate, a gel of a porous insoluble hydrous inorganic oxide filling the pores of said plate, and said separator having a porosity permitting transfer of electrolyte ions through such separator, but preventing transfer of electrode ions therethrough.

13. A battery comprising a pair of electrodes of opposite polarity and a porous separator between said electrodes for retaining electrolyte and permitting transfer of

12

electrolyte ions, said separator being composed of a porous thin rigid inert ceramic plate, a gel of hydrous zirconium oxide filling the pores of said plate, and said separator having a porosity in the range from about 5% to about 40%.

14. A battery comprising a pair of electrodes of opposite polarity and a porous separator between said electrodes for retaining electrolyte and permitting transfer of electrolyte ions, said separator being composed of a porous flame-sprayed rigid inert zirconia membrane, a gel of hydrous zirconium oxide filling the pores of said membrane and said separator having a porosity in the range from about 5% to about 40%.

References Cited

UNITED STATES PATENTS

483,692	10/1892	Lehman	136—142
2,422,045	6/1947	Ruben	136—154
2,698,305	12/1954	Plank et al.	252—317
3,056,647	10/1962	Amphlett	136—153
3,147,149	9/1964	Postal	136—163
3,276,910	10/1966	Grasselli et al.	136—86
3,257,239	6/1966	Shultz et al.	136—86
3,266,940	8/1966	Caesar	136—86

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U.S. Cl. X.R.

136—146, 153

1

3,498,840
SEPARATOR FOR ALKALINE BATTERIES AND METHOD OF MAKING SAME
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 No Drawing. Filed Nov. 2, 1967, Ser. No. 679,980
 Int. Cl. H01m 3/02; C08f 15/18
 U.S. Cl. 136-6 10 Claims

ABSTRACT OF THE DISCLOSURE

This invention relates to the preparation of membranes suitable for use as separators in concentrated alkaline battery cells by selective solvolysis of copolymers of methacrylate esters with acrylate esters followed by addition of a base and to the resultant products.

ORIGIN OF THE INVENTION

The invention described herein was made in the performance of work under a NASA contract and is subject to the provision of Section 305 of the National Aeronautics and Space Act of 1958, Public Law 85-568 (72 STAT. 435; 42 USC 2457).

BACKGROUND OF THE INVENTION

The cycle life of rechargeable battery cells is limited by the tendency of the electrodes to short circuit and it is known that this tendency can be slowed down by the use of a separator membrane between the electrodes. Such a separator must have low resistance to the passage of an electrolytic current and in many applications it must also be stable against oxidation. This is particularly the case with alkaline silver-zinc or silver-cadmium cells, the silver oxide in such cells being a powerful oxidizing agent. For this reason, separators heretofore used have not proven satisfactory since cells of only a very limited cycling life can be obtained.

Attempts to use membranes of polyacrylic acid which is known to be extremely resistant to oxidation and whose inherent polarity makes it compatible with concentrated alkali and which is receptive, in association with said alkali, to the passage of an electrolytic current have not been successful since polyacrylic acid as a membrane is soluble in alkali. One effective way of exploiting the advantageous inherent properties of polyacrylic acid is to incorporate it into a film with an insolubilizing polymer such as methyl cellulose. While such formulations do possess a high degree of resistance to oxidation, the methyl cellulose combination is not as oxidation-resistant as polyacrylic acid by itself.

SUMMARY OF THE INVENTION

It has now been found that certain copolymers of methacrylate esters with acrylic acid form membranes that possess the required combination of properties, namely, extreme oxidation resistance, insolubility in concentrated aqueous alkali, and high conductivity of an electrolytic current when in equilibrium with battery alkali.

The instant invention comprises the method of making these copolymers by first copolymerizing a methacrylate ester (or esters) with a more readily hydrolyzable ester, followed by a selective saponification whereby the methacrylate ester moieties remain essentially intact and the readily hydrolyzable ester moiety is saponified and to the partial or complete neutralization of the relatively brittle copolymer acid with a base to make membranes which are sufficiently flexible in the dry state so that they may be wrapped around electrodes without damage by handling.

2

The invention also comprises the resultant membranes and to electrochemical cells utilizing said membranes.

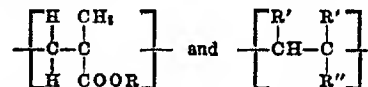
DETAILED DESCRIPTION

In carrying out the method of this invention, the copolymer is prepared by copolymerizing a methacrylate ester and a more easily-hydrolyzable monomer copolymerizable therewith selected from the group consisting of esters of C₁-C₈ alkyl alcohols with an alpha-beta unsaturated acid. The proportion of copolymerizable easily hydrolyzable monomer may be 10 to 60 mole-percent of the total ester monomers, and preferably 15 to 50 mole-percent, in the copolymer.

As to materials, the methacrylate ester used may be the reaction product of any C₁ to C₈ alkyl alcohol, preferably C₁ to C₄, with methacrylic acid. Example of suitable alcohols are methanol, ethanol, propanol, and butanol.

The copolymerizable monomer is preferably again the reaction product of a C₁ to C₄ alkyl alcohol with acrylic acid although other alpha-beta unsaturated acids such as itaconic, maleic, or fumaric can be used.

The copolymer prepared is then subjected to saponification conditions, i.e., treated with an excess of alkali (such as ammonium hydroxide, sodium hydroxide, and the like) at 100 C. or less. Under such conditions only the easily hydrolyzable ester is substantially saponified and the hydrolyzed polymer thus contains the following units randomly distributed throughout the copolymer within the molar ratios noted:



wherein R is C₁-C₈ alkyl group, R' is hydrogen or carboxylate ion, and R'' is hydrogen, carboxylate, or carboxylate methyl ion. It is understood that the cation portion of the saponifying alkali is a counter ion to the negative carboxylate or carboxylate methyl ion.

By this means it has been found possible to produce polymers containing a much higher proportionality of carboxyl groups than it is possible to obtain by direct copolymerization of methacrylate ester with acrylic acid, it being well known in the art of copolymerization of olefinic monomers that great difficulty is encountered in the incorporation of substantially molar proportions of acrylic or substituted acrylic acids with acrylate or methacrylate esters.

One advantage of this procedure is that a controllable range of polarity can be accomplished by synthetic means as opposed to the use of materials of the prior art which have a fixed polarity range. Thus, it appears possible to control the ratio of the acid moiety in the copolymer to correspond to optimum electrolytic conduction of any concentration of alkali, from 20% to 50%, potassium hydroxide for example.

Following saponification of the methacrylate-acrylate copolymers the hydrolyzed product may be recovered in acid form. For this purpose the saponification product is added to aqueous mineral acid with stirring. We have found that the acid form of the hydrolyzed copolymers is much less soluble in water than the alkaline form. Precipitation occurs and the acid form of copolymer can be readily recovered by filtration and washing.

For purposes of laying down the films of this invention it is preferred to neutralize or partially neutralize the acid form by the addition of a suitable base. It has been surprisingly found that the relatively brittle copolymer acid is converted by this neutralization to a material sufficiently flexible in the dry state that it may be wrapped with ease around electrodes without damage

3

by handling. The base used for the said neutralization may include potassium hydroxide, sodium hydroxide, tetramethylammonium hydroxide, ammonia, substituted amines such as methylamine, ethylamine, dimethyl amine, propylamine, ethanolamine, triethanolamine, propylamine, aniline, pyridine and quinoline. Preferred bases are hydroxy propylamine and triethanolamine.

The aqueous solution may be cast in sheet form and evaporated to dryness. Other forms may be made as for example plates, slabs, "buttons," films and the like. Solutions should not be so concentrated as to precipitate the components before drying.

Good flexibility in the film is of particular importance in the construction of the individual battery cells during the operation of wrapping the separators around the electrodes. In one common technique a so-called U wrap is made whereby two positive electrodes are placed butt end to butt end on a sheet of separator and after, for example, six wraps of the pair the wrapped assembly is folded at the junction in the form of the letter U. When separators of poorer flexibility are used cracks tend to occur in the separator at the base of the U, particularly in the outer wraps, thus destroying the utility of the separator at these points. We have found experimentally that this is particularly likely to occur below a certain critical threshold of flexibility, corresponding to withstanding at least about 800 flex cycles as measured by the ASTM Folding Endurance Test D643-43 with 200 grams tension on the specimen.

The invention will be further described in connection with the following examples which are set forth for the purpose of illustration only and wherein proportions are in parts by weight unless specifically stated to the contrary.

EXAMPLE 1

To a one liter resin flask equipped with stirrer, reflux condenser, heater, addition apparatus and nitrogen purge the following were charged:

Benzene (distilled over sodium) -----ml-- 500
Methyl methacrylate -----grams-- 100 (1 mol)
Ethyl acrylate -----do----- 100 (1 mol)
Azobisisobutyronitrile -----gram-- 0.2

After purging with nitrogen the benzene was brought to reflux. After 2 hours 25 ml. benzene containing 0.2 grams azobisisobutyronitrile was added and the reaction held at 75° C. for a total of 19 hours. At the end of this time a solids determination showed 29.6% of nonvolatiles which corresponded to a conversion to polymer of about 94%.

The reaction mixture was cast as a thin film on a large foil tray in the fume hood. This was removed from the foil and vacuum dried to constant weight at 50° C. for 6 hours.

By saponification a sample consumed standard alkali corresponding to 4.22 ml. N/1 per gram of polymer. This corresponded to 42.2 mol percent of the ester groups present.

EXAMPLE 2

64 grams of the copolymer ester of Example 1 were saponified by heating on a steam bath with 2500 ml. isopropanol, 925 ml. water and 52 grams of 30% KOH for 18 hours. The isopropanol was then distilled off and the resulting aqueous solution was added slowly to 200 ml. of water containing 10 ml. concentrated sulfuric acid. A white fibrous solid precipitated out. This was filtered off and washed repeatedly with cold water.

The white solid was first air-dried, then vacuum dried for several hours at 154° F. to constant weight. The yield of dry product was 47.2 grams. This represented a conversion, of copolymer ester to partially hydrolyzed ester, of 83.7% based on the prognosticated degree of hydrolysis of the analytical saponification of Example 1.

A sample of the acidic polymer was dissolved in

4

aqueous methanol and titrated with 5 N NaOH. This gave a value of 4.8 ml. N/1 per gram of polymer and corresponded to 42.3 mol percent hydrolysis of the copolymer ester to free acid groups.

Analysis of the product for carbon and hydrogen:

Element	Wt. percent	Equiv. to combined acrylic acid, mol percent
C	55.6	44.0
H	7.25	30.8
O	37.15	42.3

¹ By difference.

EXAMPLE 3

One gram of the acidic polymer of Example 2 was dissolved in 9 ml. water by solubilizing with 1 ml. of reagent ammonia. A film was cast from this solution using a doctor blade on a levelled glass plate. Upon drying a thin film formed on the glass which was too brittle to remove, shattering into small pieces when scraped. It is believed that the dried film was of substantially the same composition as the original acid polymer of Example 2, having reverted by evaporation of ammonia to the precursor acid polymer.

EXAMPLE 4

One gram of the acidic polymer of Example 2 was dissolved in 4 ml. water by solubilizing with 0.45 gram 3-hydroxypropylamine, an amount stoichiometrically equivalent to the acid groups present. The solution was cast at 22 mils clearance as in Example 3. The dried film measured 1.5 mils in thickness. It was very flexible and slightly tacky, showing a tendency to stick to itself when pressure was applied. It was insoluble in 45% KOH and in this medium showed a specific resistance of 7.2 ohms-cm. of swollen thickness. This low electrolytic resistance was somewhat below that of an unplasticized cellophane film (PUDO 119) such as is currently used for batteries, the comparison value for the latter being 9.8 ohms-cm. of swollen thickness.

EXAMPLE 5

Ten grams of the acid polymer of Example 2 was dissolved in 130 ml. water solubilized with 2.25 grams 3-hydroxypropylamine, an amount stoichiometrically equivalent to half the acid groups of the polymer, plus 10 ml. reagent ammonia, an excess over the total acid groups present. The solution was cast at 30 mils clearance on the doctor blade to give a dried film of 1.6 mils thickness. This film was of a flexibility and softness intermediate between that of Examples 3 and 4, being neither sticky nor brittle. It gave a flex test of 2368 cycles before breaking (MIT Flex Test ASTM D643-43). The tensile strength of the film was 2390 p.s.i. and the percent elongation at break 189%. The specific resistance of the film was 26 ohms-cm. in 45% KOH.

EXAMPLE 6

Two grams of the acid polymer of Example 2 were dissolved in 27 ml. water by solubilizing with 1.45 ml. 30% KOH. This amount of KOH corresponded to a stoichiometric equivalent of the acid function. The 1.4 mil film cast from this solution was hard and flexible, giving an average of 12,566 cycles in the ASTM fold test. Tensile strength was 2340 p.s.i. Resistance in 45% KOH was 35.7 ohms-cm.

EXAMPLE 7

Two grams of the acid polymer of Example 2 were dissolved in 27 ml. water by solubilizing with .74 gram triethanolamine (0.5 equivalent) and 1.7 ml. reagent ammonia. The 1.7 mil film prepared by casting this solution was hard and flexible (5741 cycles in the ASTM fold test). Resistance in 45% KOH was 35.7 ohms-cm.

The cells in which the membrane can be used are

3,498,840

5

the silver-zinc, silver-cadmium, or other like alkaline cells.

It will be understood that it is intended to cover all changes and modifications of the examples of the invention herein chosen for the purpose of illustration which do not constitute departures from the spirit and scope of the invention.

What is claimed is:

1. The method of making an oxidation resistant, highly conductive battery separator membrane comprising the steps of copolymerizing (a) a C_1-C_8 alkyl ester of methacrylic acid and (b) a readily hydrolyzable C_1-C_8 alkyl ester of an alpha-beta unsaturated acid which ester is more readily hydrolyzable than said methacrylic ester, selectively saponifying said copolymer so as to substantially saponify all of said readily hydrolyzable moiety in the copolymer without any substantial saponification of said methacrylic acid moiety, and forming the thus saponified polymer into a membrane.

2. The method of claim 1 wherein ester (a) is methyl methacrylate, ester (b) is ethyl acrylate and the copolymer contains from about 10 to about 60 mol-percent of ethyl acrylate.

3. The method of claim 1 wherein the saponified copolymer is converted to the acid form by contact with an acid prior to formation of the membrane.

4. The method of claim 3 wherein the acid form of the copolymer is at least partially neutralized by a base prior to formation of the membrane.

5. A battery separator for alkaline electrochemical cells comprising the membrane made according to the process of claim 1.

6

6. A battery separator for alkaline electrochemical cells comprising the membrane made according to the process of claim 3.

7. A battery separator for alkaline electrochemical cells comprising the membrane made according to the process of claim 4.

8. An alkaline electrochemical cell comprising electrodes, a concentrated aqueous alkali fluid, and the battery separator of claim 5 interposed between the electrodes.

9. An alkaline silver cell comprising electrodes, a concentrated aqueous alkali fluid, and the battery separator of claim 6 interposed between the electrodes.

10. An alkaline silver-zinc cell comprising a silver electrode, a zinc electrode, a concentrated aqueous alkali fluid, and the battery separator of claim 7 interposed between the electrodes.

References Cited

UNITED STATES PATENTS

3,284,382	11/1966	Rosser et al.	136-146 XR
3,330,702	7/1967	Horowitz	136-146
3,376,168	4/1968	Horowitz	136-146

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[54] **BATTERY SEPARATOR**
4 Claims, No Drawings

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[50] Field of Search 136/146,
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[56] **References Cited**
UNITED STATES PATENTS

2,482,062 9/1949 Hanson 136/146

2,965,697	12/1960	Duddy.....	136/146
3,092,519	6/1963	Olson	136/146
3,101,276	8/1963	Hendricks	117/56
3,111,424	11/1963	LeClair	117/93.31 X
3,186,876	6/1965	Piechon.....	136/143
3,188,165	6/1965	Magat et al.....	117/93.31 X
3,216,864	11/1965	Bushrod et al.....	136/148
3,240,723	3/1966	Friedlander.....	260/2.1
3,330,702	7/1967	Horowitz.....	136/146
3,427,206	2/1969	Scardaville et al.....	136/146

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ABSTRACT: A battery separator for alkaline storage batteries of the nonwoven fiber mat type; the fiber mat being impregnated with a polymeric binder and a monomeric wetting agent, the thus impregnated mat being subjected to irradiation to form a cross-linked unitary structure.

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BATTERY SEPARATOR**BACKGROUND OF THE INVENTION**

Storage batteries of the alkaline type, such as those utilizing a potassium hydroxide electrolyte, have their operational efficiency severely circumscribed by the nature of the separator elements used in the battery.

Various separator elements have been proposed including the fiber mat-type having various binder impregnants. It has been found that with known separator elements, high rate charging may be adversely affected; migratory phenomena within the cell may become excessive to thereby reduce the efficiency of the device, and other battery characteristics such as holding a charge, the discharge curve, etc., may be relatively poor.

Accordingly, an object of this invention is to provide an improved fiber mat battery separator which increases the efficiency of battery charge and discharge.

Another object of this invention is to provide an improved battery separator of the character described, wherein the fibers of the mat and impregnating agents for the mat are selected so that upon suitable irradiation of the impregnated mat, a cross-linking action takes place as between the several constituents of the mat, to produce a unitary structure having improved properties as they relate to usage in alkaline storage batteries.

Other objects of this invention will in part be obvious and in part hereinafter pointed out.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In accordance with the instant invention, a nonwoven fiber mat is formed from selected polymeric fibers of suitable denier and staple length; the mat then being impregnated with an aqueous solution of a polymeric unsaturated organic acid; the impregnated web being then hot calendared to a desired thickness and sprayed with a solution of a monomeric unsaturated organic acid-wetting agent. The thus impregnated web is subjected to selected conditions of irradiation to produce cross-linking effects and unitizing the web.

Thus, by way of illustration, a battery separator web of the instant invention was made as follows:

A nonwoven fiber web was formed on a Curlator Rando-Webber or other web forming equipment, utilizing polypropylene fibers of 3 denier, 1 9/16 inches staple length. The web is then saturated with an aqueous solution of polyacrylic acid, which is used in amounts to constitute 5 percent by weight of the completed article.

The saturated web is then calendared by a stand of heated calendar rolls to a thickness of about 8 mils. The material

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weight is about 2 ounces per square yard.

The calendared web is then sprayed with an aqueous solution of acrylic acid, in an amount such that the residual acid in the finished product amounts to about 5 percent by weight thereof.

The impregnated and coated web is then subjected to a 7 Mev linear accelerator to produce an irradiation of about 2 megarads. The resultant product is then converted to battery separator elements in a manner known in the art.

It has been found that the use of battery separators of the instant invention, the efficiency of alkaline-type storage batteries using potassium hydroxide electrolyte, as in a nickel-cadmium battery, is substantially improved and such battery is remarkably free of adverse migration phenomena and the like.

It is understood that in lieu of polypropylene fibers, polyethylene or polyamid fibers may be used. Also, the denier of the fibers may range from about 1.5 to about 15.

The web impregnant may be constituted of polymeric unsaturated organic acids such as polymethacrylic acid and polyitaconic acid in lieu of polyacrylic acid. The binder concentration may range from about 2 percent to about 15 percent based on the total weight of the finished product.

In place of the acrylic acid-wetting agent, other unsaturated organic acid monomers may be used, such as methacrylic acid and the like. The monomer can be combined with a trace amount (1 to 5 percent by weight) of a monofunctional monomer such as divinylbenzene to reduce the radiation dosage for the cross-linking action.

While the irradiation is preferably of the order of 1 to 2 megarads; the range may be from about 0.5 to 25 megarads.

I claim:

1. A battery separator for alkaline storage batteries comprising a nonwoven, matted web of polymeric fibers selected from the group consisting of polypropylene, polyethylene and polyamide, a polymeric saturant distributed through said web, said saturant being selected from the group consisting of polyacrylic acid, polymethacrylic acid and polyitaconic acid, and a coating on said saturated web, said coating being selected from the group consisting of acrylic acid and methacrylic acid, said saturant and coating being irradiated in situ to provide a cross-linking of the fibers, saturant and coating.

2. A battery separator as in claim 1 wherein said fibers are of polypropylene having a 3 denier and a staple length of about 1.5 to about 2.0 inches.

3. A battery separator as in claim 1 wherein said fibers have a denier of from about 1.5 to about 10.0.

4. A battery separator as in claim 1, wherein said saturant amounts to about 5 percent by weight of the irradiated web.

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